VOL. XXXIV. AUGUST, 1905. NO. 2.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

THE TITRATION OF FERROUS IRON WITH PERMANGANATE IN THE PRESENCE OF HYDROCHLORIC ACID.

BY GREGORY PAUL BAXTER AND HARRY LOUIS FREVERT.

Recent investigation in this laboratory upon the titration of oxalic acid with potassium permanganate, in the presence of hydrochloric acid, has shown that this operation may be accurately performed without the addition of manganous salts, provided the temperature of the solution of oxalic acid, at the beginning of the titration, is above 70°.[1] With the idea that a similar procedure might be successfully applied to the titration of ferrous iron, under the same conditions, the following experiments were carried out:

A solution of ferrous chloride, containing approximately 0.01 gram in 1 cc., was prepared by reducing ferric chloride with iron wire, in the presence of hydrochloric acid. The

[1] Baxter and Zanetti: THIS JOURNAL, 33, 500 (1905).

solution contained sufficient hydrochloric acid for the subsequent oxidation of the iron. Potassium permanganate solutions used in the oxidation contained, approximately, 4 grams of salt per liter.

The relative strengths of the ferrous chloride and permanganate solutions were determined by slowly adding permanganate, from a burette, to 25 cc. portions of the ferrous solution, which had been diluted to 150 cc. by introducing the ferrous chloride, from a pipette, into the requisite amount of a boiling solution of 1 gram of manganous chloride crystals. It has already been shown, by various experimenters, that potassium permanganate may be used for the accurate estimation of iron, in the presence of hydrochloric acid, provided the solution contains sufficient manganous salt.[1]

In order, as far as possible, to avoid oxidation of the ferrous solution by the air, the titrations were performed in Erlenmeyer flasks. Since, even in the cold, the ferrous solution slowly changed in strength, comparisons of the permanganate and ferrous chloride were always made immediately before the use of the solutions. The change of color from the yellow of the ferric solution to the purplish-yellow, due to the presence of an excess of permanganate, is sharp and affords a very satisfactory end-point; but, even for a practised eye, a "standard end-point" makes the change more easily detected.

Titrations were first made to determine whether, in the case of iron as in the case of oxalic acid, the amount of permanganate required was dependent upon the temperature. In each experiment the ferrous solution was diluted by addition to warm or hot freshly boiled, distilled water. In analyses 10 and 11 the solution was heated to boiling subsequently to dilution with boiling water. No manganous salt was added in any case. The recorded temperature is that at the beginning of the titration. In all the experiments below 70° a distinct odor of hypochlorous acid was perceptible.

[1] Kessler: Ann. Phys., 194, 48 (1863); 198, 225 (1863); Zimmermann: Ann. Chem. (Liebig), 213, 305 (1882); Wagner: Z. physik. Chem., 28, 60 (1899); Gooch and Peters: Am. J. Sci., 7, 461 (1899).

Table I.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
1	150	30	37.52	37.16	1.0
2	"	30	37.58	"	1.1
3	"	29	37.48	"	0.9
4	"	58	37.41	"	0.7
5	"	69	37.35	"	0.5
6	"	78	37.30	"	9.4
7	"	85	37.26	"	0.3
8	"	85	37.25	"	0.2
9	"	88	37.24	"	0.2
10	"	97	37.29	"	0.3
11	"	100	37.28	"	0.3
12	"	85	39.59	39.51	0.2
13	"	84	39.60	"	0.2
14	"	81	39.94	39.85	0.2
15	"	85	39.97	"	0.3
16	"	83	39.96	39.76	0.5

It is evident, from the above results, that the error increases with diminishing temperature, as in the case of oxalic acid,[1] but that, even at the highest possible temperatures, the excess of permanganate required amounts to between 0.2 and 0.3 per cent.

With the hope that increasing the volume of the ferrous solution might have a beneficial effect, several titrations were performed where the volume of the ferrous solution was both greater and less than 150 cc. In analyses 17, 18 and 19 the solution was heated to the recorded temperature, after dilution.

Table II.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
17	50	87	36.86	36.77	0.2
18	50	95	36.89	"	0.3
19	100	97	36.87	"	0.3
20	300	87	36.85	"	0.2

These experiments show that the dilution is without effect upon the magnitude of the error.

It was to be expected that the error would increase with in-

[1] *Loc. cit.*

creasing hydrochloric acid concentration. Contrary to expectation the quantities of permanganate used were slightly smaller when a considerable excess of hydrochloric acid (sp. gr. 1.04–5) was added before titration. When more than 40 cc. were employed the end-point became uncertain.

Table III.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	HCl added. cc.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
21	150	83	. .	36.02	35.86	0.4
22	"	85	. .	36.00	"	0.4
23	"	"	. .	36.02	"	0.4
24	"	"	10	36.00	"	0.4
25	"	"	20	36.02	"	0.4
26	"	"	20	36.02	"	0.4
27	"	"	30	36.03	"	0.5
28	"	"	30	36.02	"	0.4
29	"	"	40	35.93	"	0.2
30	"	"	40	35.95	"	0.3
31	"	"	30	39.11	39.02	0.2
32	"	"	30	39.10	"	0.2
33	"	"	40	39.10	"	0.2
34	"	"	40	39.10	"	0.2
35	"	"	. .	39.20	"	0.5
36	"	"	. .	39.18	"	0.4

Finally, the effect of varying temperature and dilution, in the presence of varying amounts of both manganous sulphate and chloride, was determined (see Table IV., on opposite page).

From the results of the above experiments it can be seen, first, that neither the temperature of the solution nor the dilution is important if sufficient manganous salt is present; secondly, that although, at 97°, 0.5 gram of crystallized manganous chloride is sufficient to prevent loss of chlorine, at lower temperatures accurate results can be obtained only in the presence of at least 1 gram of this salt; and, finally, that manganous sulphate is more effective than manganous chloride in preventing the error, 0.5 gram of the former being sufficient at a dilution of 150 cc., at 85°.

In the previous paper upon the titration of oxalic acid in the presence of hydrochloric acid, the hypothesis was advanced

Table IV.

Number of analysis.	Volume of solution.	Temperature.	$MnCl_2.4H_2O$ added.	$MnSO_4.5H_2O$ added.	$KMnO_4$ used.	$KMnO_4$ theory.	Error.
	cc.	Degrees.	Grams.	Gram.	cc.	cc.	Per cent.
37	150	30	1.0		37.17	37.16	0.0
38	"	29	"		37.16	"	0.0
39	"	84	"		37.17	"	0.0
40	"	83	"		37.15	"	0.0
41	"	85	"		37.15	"	0 0
42	300	88	"		36.78	36.77	0.0
43	50	93	"		36.76	"	0.0
44	"	92	"		36.77	"	0.0
45	100	94	"		36.77	"	0.0
46	150	80	0.5		39.48	39.51	—0.1
47	"	83	"		39.51	"	0.0
48	"	84	"		39.51	"	0.0
49	"	83	"		39.92	39.76	0.4
50	"	85	"		39.91	"	0.4
51	"	85	"		39.10	39.02	0.2
52	"	85	"		39.10	"	0.2
53	"	85	"		39.10	"	0.2
54	"	97	"		37.17	37.16	0.0
55	"	97	"		37.16	"	0.0
56	"	85	1.0		39.73	39.76	—0.1
57	"	80	2.0		39.75	"	0.0
58	"	85	3.0		39.79	"	0.1
59	"	85	4.0		39.76	"	0.0
60	"	80	1.0		39.82	39.84	—0.1
61	"	82	2.0		39.83	"	0.0
62	"	81	3.0		39.86	"	+0.1
63	"	85	1.0		36.88	36.77	0.3
64	"	87	1.0		36.93	"	0.4
65	"	85	1.0		36.68	"	—0.2
66	"	85	2.0		36.80	"	0.1
67	"	85	2.0		36.75	"	—0.1
68	"	82	2.0		36.77	"	0.0
69	"	86	3.0		36.75	"	—0.1
70	"	86		0.5	36.74	36.73	0.0
71	"	85		0.5	36.73	"	0.0
72	"	86		1.0	36.73	"	0.0
73	"	87		0.5	34.73	34.70	0.1
74	"	86		0.5	34.70	"	0.0
75	"	87		0.5	34.70	"	0.0
76	"	87		0.5	34.71	"	0.0
77	"	86		1.0	34.71	"	0.0
78	"	87		1.0	34.70	"	0.0

that, at low temperatures, the use of an excess of permanganate over that theoretically necessary is due to the volatilization of hypochlorous acid, produced by the action of the permanganate upon the hydrochloric acid; and that, at high temperatures, this loss is prevented by the more rapid action of the permanganate upon the manganous salts, produced by the reduction of the permanganate, to form compounds of trivalent or quadrivalent manganese which, in turn, are capable of rapidly oxidizing the oxalic acid. In the course of the present investigation additional evidence was obtained which supports this hypothesis.

In the first place it was shown that permanganates may be formed by the interaction of hypochlorites and manganous salts, by bringing together calcium hypochlorite and manganous chloride, in the presence of much alkali. Since acids accelerate the reduction of potassium permanganate by chlorides, alkalies should hasten the reverse process. To a concentrated solution of manganous chloride much sodium hydroxide and calcium hypochlorite were added. The pasty mass was then heated upon the steam-bath for some time. When the product was diluted a solution of sodium permanganate, of considerable concentration, was obtained. That this permanganate was not due to possible chlorates from the transformation of the hypochlorites was certain, since a repetition of the experiment, with potassium chlorate in place of the calcium hypochlorite, gave no trace of permanganate.

Although this proof that the possible reaction of permanganate upon hydrochloric acid, to produce hypochlorous acid, is reversible, does not make it absolutely certain that the reduction of the permanganate actually takes place in this way, a few simple experiments gave positive evidence that this is the case. To separate solutions of oxalic acid and ferrous sulphate, at room temperature, strong, concentrated chlorine water was added. When tested with starch iodide paper, after a few seconds, not even a trace of chlorine could be detected. On the other hand, when a solution of calcium hypochlorite was added to similar solutions of oxalic acid and ferrous sulphate, both of which had been made acid with hydrochloric acid, the

odor of hypochlorous acid was marked and persistent for some time, although, eventually, the hypochlorous acid was reduced in both cases. Obviously, since chlorine is taken up almost instantly by both oxalic acid and ferrous sulphate, in the latter experiment the solutions could not have contained free chlorine. The odor which is plainly perceptible at the beginning of titrations, at low temperatures, with permanganate in the presence of hydrochloric acid must, therefore, be due to hypochlorous acid and not to chlorine, as is commonly assumed.

On the other hand, manganous salts were found to have no appreciable effect. For, when acid solutions of oxalic acid and ferrous sulphate, to both of which manganous sulphate had been added, were treated with calcium hypochlorite, hypochlorous acid could be detected for the same length of time as with solutions, otherwise exactly similar, but containing no manganous sulphate. Since the oxidation by hypochlorous acid takes place at the same rate whether manganous salts are present or not, it is evident that the beneficial effect of manganous salts, in titrations with permanganate, is due to acceleration of the reaction of the *permanganate* upon the manganous salts, as proposed originally by Zimmermann,[1] and subsequently maintained by other investigators,[2] as well as in this paper.

Upon heating the solutions of oxalic acid and ferrous sulphate, containing hypochlorous acid, the hypochlorous acid disappeared by reduction and, when calcium hypochlorite was added to hot acid solutions of the reducing agents, the reaction was practically instantaneous.

Experiments 21 to 36, in which it was found that, up to a certain point, increasing the concentration of the hydrochloric acid diminishes the error, indicate that, under these conditions, the reaction between hypochlorous and hydrochloric acids to produce chlorine is considerably accelerated.

The above experiments show, conclusively, that the loss of

[1] Ann. Chem. (Liebig), 213, 305 (1882).

[2] Wagner: Z. physik. Chem., 28, 1 (1899); Gooch and Peters: Am. J. Sci., 7, 461 (1899).

chlorine, during titrations with permanganate in the presence of hydrochloric acid, together with the consequent positive error in the quantity of permanganate employed, is not due to volatilization of free chlorine from the solution, but to the formation and volatilization of hypochlorous acid. The catalytic effect of manganous salts is the result of the production of some intermediate manganic compound, through the action of the permanganate. Finally, the oxidation of oxalic acid and ferrous iron, under the conditions which have been described, takes place chiefly through the agency of the above-mentioned manganic compound, although, undoubtedly, both permanganate and hypochlorous acid are capable of acting directly upon either oxalic acid or ferrous salts. Obviously the rate of oxidation is dependent upon the velocities of all the reactions involved. In the case of oxalic acid, even without the addition of manganous salts, it has been found possible, by the use of high temperatures, to accelerate the Guyard reaction of permanganate upon manganous salts to such an extent as to avoid appreciable formation and loss of hypochlorous acid by volatilization. Unfortunately, in the case of ferrous salts, a similar remedy was found to give less satisfactory results.

Summary.

The results of the foregoing research are, then, as follows:

1. It is found that, even at the highest possible temperatures, the accurate estimation of ferrous iron, by titration with permanganate, in the presence of hydrochloric acid, is impossible without the introduction of manganous salts.

2. The results obtained at 80°–90° are however, about 0.3 per cent. too high, so that titrations carried out in this fashion may be corrected, with considerable exactness, by applying a negative correction of 0.3 per cent., if the concentration of the hydrochloric acid is not too great.

3. It is found that, except at temperatures in the neighborhood of 95°, 0.5 gram of manganous chloride is insufficient completely to eliminate the error, but that 1 gram of this salt

yields accurate results at all temperatures. On the other hand, 0.5 gram of manganous sulphate is a sufficient quantity.

4. The hypothesis previously proposed that, in the titration of oxalic acid and ferrous iron, in hydrochloric acid solution, by permanganate, the error, in the absence of manganous salts, is due to the production of hypochlorous acid and volatilization of this substance from the solution, receives further support.

CAMBRIDGE, MASS.,
April, 26, 1905.

Contributions from the Sheffield Laboratory of Yale University.

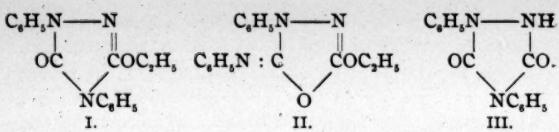
CXXIV.—ON SOME URAZOLE AND IMIDOTHIOBIAZOLINE DERIVATIVES.

BY HENRY L. WHEELER AND JOANNES G. STATIROPOULOS.

In a paper on phenylthiosemicarbazidic esters, which was published five years ago, Wheeler and Dustin described the preparation of three compounds of unknown constitution. Two of them were provisionally represented as imidothiobiazolines, the other as a urazole derivative.[1] Further work on the structure of these compounds has now established the fact that the so-called biazoline derivatives are really urazoles, while the compound described as a urazole in all probability is an imidothiobiazoline. In the study of the somewhat confusing reactions which lead either to an imidobiazoline or a triazole condensation we have also been impressed with the fact that little can be expected from analogy.

The first compound to be considered was originally obtained by combining phenyl isocyanate with ethyl phenylthioncarbazinate $C_6H_5NH.NHCS.OC_2H_5$, this gave ethyl *c,b*-diphenyl-*α*-thionsemicarbazidate, $C_6H_5NHCO(C_6H_5)N.NHCS.OC_2H_5$. When this substance was treated with sodium ethylate, with or without ethyl bromide, a compound melting at 86° resulted, which was free from sulphur. This, on analysis, gave results agreeing with the calculated for 1,4-diphenyl-3-ethoxyurazole, I, or *α*-ethoxy-*α'*-phenylimido-*β'*-phenyloxybiazoline II.

[1] THIS JOURNAL, 24, 430 (1900).



I. II. III.

We have now found that the substance gives 1,4-diphenylurazole, III, melting at 163°, when boiled with hydrobromic acid, the product being identical with the compound described by Busch and Holzmann[1] and later obtained by other methods,[2] notably by desulphurizing 1,4-diphenyl-5-thiourazole[3] with potassium permanganate.

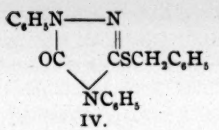
We have prepared the substance represented by Formula I by treating the silver salt of 1,4-diphenylurazole with ethyl bromide and we find that it is identical with the material melting at 86°, described in our previous paper.

This shows that the substance is a triazole, or rather a urazole, because it excludes the possibility that the material is a biazoline which, on hydrolysis, rearranges to the diphenylurazole.

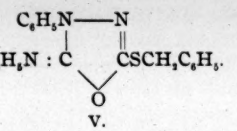
We did not obtain this 1,4-diphenyl-3-ethoxyurazole on treating the sodium salt of the urazole with ethyl bromide, at 100°, but found instead that an isomeric nitrogen derivative resulted. It is, therefore, probable that Busch's corresponding methyl derivative,[4] prepared under similar conditions, has the alkyl group attached to nitrogen and not, as he represents, to oxygen.

The next compound prepared by Wheeler and Dustin to be considered was originally obtained by treating the above mentioned ethyl *c,b*-diphenyl-*a*-thionsemicarbazidate with aqueous alkali and benzyl chloride. This operation gave a product melting at 110°–112°, containing sulphur and which agreed in composition with a compound represented by Formula IV or V.

[1] Ber. d. chem. Ges., **34**, 341 (1901).
[2] Busch and Heinrichs: *Ibid.*, **34**, 2336.
[3] Busch: *Ibid.*, **35**, 973 (1902).
[4] *Ibid.*, **34**, 2337.

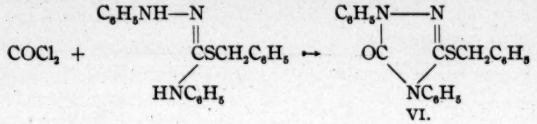


IV.



V.

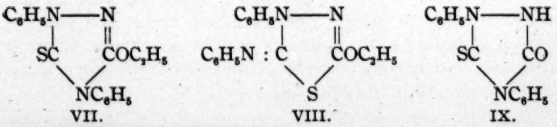
The following synthesis now proves conclusively that this substance is to be represented by Formula IV, in other words, it is 1,4-diphenyl-3-benzylmercaptourazole. Diphenylthiosemicarbazide was combined with benzyl chloride, giving diphenylpseudobenzylthiosemicarbazide hydrochloride, and this substance, with alkali and phosgene, reacted as follows:



VI.

The compound thus obtained was identical in every respect with the one obtained by Wheeler and Dustin, melting at 110°–112°.

We found when ethylphenylthioncarbazinate, $C_6H_5NH.NH.CS.OC_2H_5$,[1] was treated with phenyl mustard oil that hydrogen sulphide was evolved and a compound, melting at 83°, resulted. Analysis indicated that this was either a urazole, VII., or an imidothiobiazoline, VIII.



VII. VIII. IX.

When this substance was boiled with hydrobromic acid 1,4-diphenyl-5-thiourazole, IX, melting at 216°–221°, was obtained.[2]

Marckwald[3] and Busch and Holzmann[3] found that this sub-

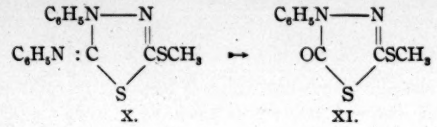
[1] Wheeler and Barnes: THIS JOURNAL, 34, 65 (1900).

[2] Marckwald: Ber. d. chem. Ges., 25, 3109 (1892); Busch, Holzmann: *Ibid.*, 34, 326; 34, 2328; 35, 974 (1902).

[3] *Loc. cit.*

stance, IX, on methylating, gave a product having the alkyl group attached to sulphur; it readily eliminated mercaptan, yielding 1,4-diphenylurazole, III. This excludes the biazoline formula for these compounds and leads to the conclusion that our compound, melting at 83°, is 1,4-diphenyl-3-ethoxy-5-thiourazole, VII.

It may be stated, in connection with the hydrolysis of the material melting at 83°, that Busch and Wolpert[1] found their "phenylthiobiazolon-anil-thiomethan" X, which has a structure analogous to VIII, did not give a urazole when boiled with hydrochloric acid. The compound yielded aniline instead, giving a thiobiazoline represented by formula XI, which shows that, in this case, the hydrolysis does not involve a molecular rearrangement.



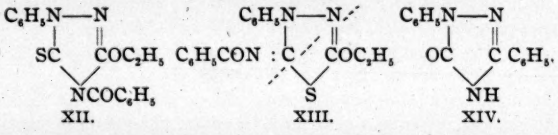
X. XI.

It is noteworthy that the compound, VII, melting at 83° and also the urazole, IX, melting at 216°–221°, were obtained together when isocyanphenyl chloride, $C_6H_5NCCl_2$ was allowed to act on ethyl phenylthioncarbazinate. According to Freund and König,[2] the action of isocyanphenyl chloride on acyl compounds of phenyl hydrazine yields biazoline derivatives. It may be added, however, that Busch and Wolpert found, according to the choice of certain conditions, either a biazolon, or a urazole could be obtained by the action of mustard oils on dithiocarbazinic acids.

The third substance of unknown constitution, described by Wheeler and Dustin, was obtained by the action of benzoyl isothiocyanate, C_6H_5CONCS, on ethyl thioncarbazinic ester. Hydrogen sulphide was evolved and a compound melting at 138° resulted. This agreed in composition with the urazole, XII, or the imidothiobiazoline, XIII. From analogy to the above,

[1] Ber. d. chem. Ges., **34**, 306 (1901).
[2] *Ibid.*, **26**, 2869 (1893).

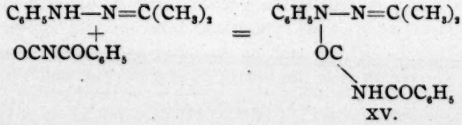
that is the behavior of phenyl isothiocyanate towards ethyl phenylthioncarbazinic ester, this compound should be a urazole, but the properties of the substance which have now been determined are not reconcilable with this view.



XII. XIII. XIV.

With the expectation of obtaining 1-phenyl-5-thiourazole we boiled the substance, melting at 138°, with hydrobromic acid. A product, free from sulphur, was obtained. This agreed in composition with a diphenyloxytriazole. It melted at 229°–230° and, therefore, was not identical with the known 1,5-diphenyl-3-oxytriazole described by Young.[1] The new isomer, or 1,3-diphenyl-5-oxytriazole, XIV, was prepared and it was then found that this was the material which resulted from the hydrolysis with hydrobromic acid. Since the urazole ring is very stable towards acids, this curious behavior, which, in either case, involves a rupture of the ring and a subsequent condensation, is best explained by the biazoline structure, XIII., the cleavage taking place as shown by the dotted line

The new 1,3-diphenyl-5-oxytriazole was prepared by combining benzoyl isocyanate, C_6H_5CONCO[2] with acetone phenylhydrazone. The resulting benzoylphenylsemicarbazone, XV, on warming with a little dilute hydrochloric acid, evolved acetone and condensed, forming the triazole melting at 229°–230°.



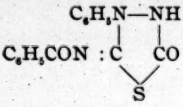
XV.

When the compound melting at 138°, prepared by Wheeler and Dustin, was melted in a stream of dry hydrogen chloride,

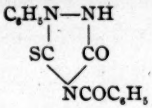
[1] J. Chem. Soc., **67**, 1064 (1895).

[2] Billeter: Ber. d. chem. Ges., **36**, 3218 (1903).

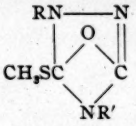
ethyl chloride was given off and a compound agreeing in composition with the imidobiazolon, XVI, or the urazole, XVII, was obtained. This melted at 206°.



XVI.



XVII.

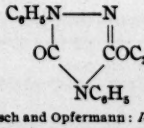


XVIII.

Busch[1] has shown that compounds, such as IX or XVII, that is to say 1,4-disubstituted-5-thiourazoles, on methylation, give thioethers. These are represented by Formula XVIII, in which the alkyl group is attached to sulphur. This is evident from the fact that they readily separate mercaptan. We find that our material, on alkylating with ethyl iodide and alkali, at 100°, does not give a thioether, but regenerates the compound melting at 138°. We conclude, from this result and from the behavior of the material on hydrolysis with hydrobromic acid, that the substance described by Wheeler and Dustin, melting at 138°, is α-ethoxy-α'-benzoylimido-β'-phenylthiobiazoline, XIII, and not a urazole derivative, while the diethylated product obtained from it, melting at 206°, is α'-benzoylimido-β'-phenylthiobiazolon, XVI. The fact that this latter substance is decomposed by boiling alkali and that 1-phenyl-4-thiourazole was not obtained, lends further support to the biazoline structure for these compounds.

The absence of analogy in the behavior of phenyl isothiocyanate and of benzoyl isothiocyanate towards ethyl phenylthioncarbazinate recalls the similar reactions of α-diphenylthiosemicarbazide with phosgene, whereby 1,4-diphenyl-5-thiourazole is formed and, on the other hand, with thiophosgene, which results in the formation of a thiobiazolon.[2]

EXPERIMENTAL.

1,4-Diphenyl-3-ethoxyurazole,  —1,4-Di-

[1] Ber. d. chem. Ges., **38**, 975 (1902); Busch and Opfermann: *Ibid.*, **37**, 2333 (1904).
[2] Busch and Holzmann: *Ibid.*, **34**, 326 (1901).

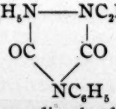
phenylurazole was prepared from phenyl isocyanate and ethyl phenylcarbazinate, as described by Busch and Heinrichs.[1] Six and one-half grams of this substance were suspended in alcohol and an alcoholic solution of 0.6 gram of sodium was added, whereupon a clear solution resulted. This was poured, with vigorous stirring, into a solution of 4.4 grams of silver nitrate, in 250 cc. of water. A fine, brownish-gray precipitate separated which was allowed to settle and was washed by decantation and then on the filter. It was dried over sulphuric acid, suspended in ether and allowed to remain with an excess of ethyl iodide, in the cold, for several days. The ether solution, on evaporation, left an oily residue which solidified. This was washed with alkali and water. On crystallizing from alcohol, long, slender, colorless prisms were obtained, which softened at 83°–85° and melted, to a clear oil, at 85°–86°.

Analysis:

	Calculated for $C_{16}H_{15}O_2N_3$.	Found.
N	14.95	15.36

This compound proved to be identical with the substance described in a previous article as α-ethoxy-α'-phenylimido-β'-phenyloxybiazoline.[2] A small sample of this material, left by Mr. Dustin, was boiled with strong hydrobromic acid for a few minutes. The acid was evaporated and the residue was boiled with petroleum ether and crystallized from alcohol. It then melted at 163° and had all the properties of 1,4-diphenylurazole.

1,4-Diphenyl-2-ethylurazole,



—Three grams of 1,4-diphenylurazole were dissolved in 1 molecular proportion of alcoholic sodium hydroxide and an excess of ethyl bromide was added. This solution was heated at 100°, for 3 hours, whereupon the contents of the tube gave a neutral reaction. The alcohol was evaporated and the

[1] Ber. d. chem. Ges., **34**, 2335 (1901).

[2] This JOURNAL, **24**, 442 (1900).

residue was treated with water; this left a reddish-colored oil, which solidified and, on crystallizing from alcohol, colorless glistening prisms were obtained, melting at 125°–126°. Analysis:

	Calculated for $C_{18}H_{13}O_2N_3$.	Found.
N	14.95	15.28

This material is readily soluble in alcohol, ether and benzene. It is moderately soluble in hot water and practically insoluble in cold. It remained unaffected when boiled with hydrobromic acid.

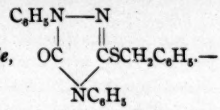
The Benzyl Chloride Addition-product of Diphenylthiosemicarbazide, $C_6H_5NHNHCCl(SCH_2C_6H_5)NHC_6H_5$. — Ten grams of finely-powdered diphenylthiosemicarbazide were moistened with dry benzene and 3.3 grams of benzyl chloride were added. The mixture was digested on the steam-bath and in a few hours all went into solution. At the end of 8–9 hours a finely divided, white powder separated. This was washed with ether, whereupon it melted at 149°–150°. The substance is readily soluble in alcohol. Analysis:

	Calculated for $C_{20}H_{20}N_3SCl$.	Found.
N	11.37	11.69

The free pseudobenzylthiosemicarbazide is very unstable. In the air it rapidly oxidizes, giving deep red solutions. When the above experiment was repeated, using alcohol as a solvent, the addition was complete in an hour. The alcoholic solution was evaporated to dryness and a light yellow, oily residue was obtained which, on cooling, hardened to a resinous mass. This was stirred with sodium hydroxide and ether and the ether was dried over calcium chloride. A portion of this solution was evaporated and a reddish, oily residue was obtained which did not crystallize satisfactorily from any solvent. By dissolving some of the benzyl chloride addition-product in alcohol, cooling in a freezing-mixture and neutralizing with dilute sodium hydroxide, at first a white turbidity resulted, then a yellowish oil, which very soon turned bright red. On remaining exposed in the freezing-mixture for several hours, a

few bright red needles were obtained, melting at about 55°. This substance, which was undoubtedly the azo derivative, $C_6H_5N : N.C(SCH_2C_6H_5) : NC_6H_5$, was not further examined.

1,4-Diphenyl-3-benzylmercaptourazole,

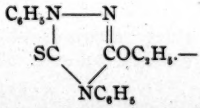


The main portion of the above ether solution of the free pseudothiosemicarbazide was shaken with a solution of phosgene in toluene and an excess of alkali. The phosgene solution being added in small portions, until it gave no precipitate in the ether. The ether and toluene were then evaporated and, on cooling, the oily residue solidified. This was crystallized several times from alcohol, when fine, long, shining needles were obtained, melting at 110°–112°. Analysis:

	Calculated for $C_{21}H_{17}ON_3S$.	Found.
N	11.69	11.55

This proved to be the substance obtained by Wheeler and Dustin, when ethyl *c,b*-diphenyl-α-thionsemicarbazidate was treated with alkali and benzyl chloride.[1]

1,4-Diphenyl-3-ethoxy-5-thiourazole,

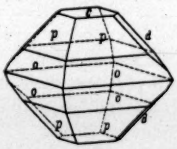


Five grams of ethyl phenylthioncarbazinate and 3.5 grams of phenyl mustard oil were heated on the steam-bath, for about 6 hours. Hydrogen sulphide was evolved and an oil resulted. On cooling in a freezing-mixture crystals separated which were washed with ether and found to be diphenylthiourea. The ether left, on evaporation, a thick, yellow oil which was extracted with dilute hydrochloric acid. This extract was neutralized with sodium hydroxide, the oil which separated, on cooling in a freezing-mixture, solidified. It was crystallized once from alcohol, then dissolved in ether and left to crystallize by spontaneous evaporation. In this manner large,

[1] THIS JOURNAL, 24, 442 (1900).

well-developed pyramids were obtained, melting at 83°. Dr. W. E. Ford has kindly furnished us with the following crystallographical description:

The crystals are orthorhombic in symmetry, showing a simple combination of base, *c* (001), two pyramids, *ρ* (111), and *o* (221), with brachydome *d* (011). Their habit is illustrated by the accompanying figure. The crystals were well



developed, having a diameter of 5 mm. The faces were somewhat etched, but gave fairly distinct signals on the reflection goniometer. The following angles were measured:

	Measured.	Calculated.
c (001) ∧ *ρ* (111)	= 55°50′ *	
c (001) ∧ *o* (221)	= 71°19′	71°34¾′
c (001) ∧ *d* (011)	= 45°20½′ *	
d (011) ∧ *ρ* (111)	= 36°50′	36°58′

Using the measurements marked by an asterisk as fundamental, the axial ratio was calculated as:

$$a : b : c = 0.9528 : 1.00 : 1.012.$$

Considering the rather poor quality of the faces the agreement between the calculated and measured angles, as indicated in the above table, is sufficiently close.

This substance was also obtained by Dr. T. B. Johnson, as follows: *Isocyanphenyl chloride* and *ethyl phenylthioncarbazinate*, 3.5 grams of the latter and 3.1 grams of the former, were mixed in dry benzene and allowed to stand at ordinary temperatures. The action took place slowly and hydrogen chloride was evolved, the solution assumed a red color and became turbid. The mixture was warmed on the steam-bath, this caused a violent effervescence, ethyl chloride and hydrogen sulphide were evolved. After the evolution of gas had ceased the

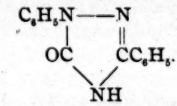
product was a thick oil. It was washed with sodium hydroxide, whereupon the oily, insoluble material solidified on standing. It crystallized from alcohol in beautiful prisms and melted at 83°. It had all the properties of the compound above mentioned. Analysis:

	Calculated for $C_{18}H_{12}ON_2S$.	Found.
N	14.14	13.88

The material is readily soluble in alcohol, less readily in ether and insoluble in water; when boiled with hydrobromic acid it gave *1,4-diphenyl-5-thiourazole*, melting at about 215°. The same substance was obtained on treating the fused material, at 85°–95°, with dry hydrogen chloride. It was also obtained as a product of the above reaction, it being removed by the treatment with alkali. Analysis:

	Calculated for $C_{14}H_{11}ON_3S$.	Found.
N	15.6	15.3

1,3-Diphenyl-5-oxytriazole,



—Three grams of the substance described by Wheeler and Dustin, melting at 136°–138°, was boiled, for about 8 minutes, with strong hydrobromic acid, whereupon crystals of benzoic acid condensed at the mouth of the flask. The acid was then evaporated to dryness on the water-bath and the residue was purified by dissolving in alkali, precipitating with hydrochloric acid and crystallizing from alcohol. This gave colorless needles, melting at 229°–230°. The solubility of the compound in alkali and its melting-point suggested that we had obtained the expected 1-phenyl-5-thiourazole, but our substance proved to be free from sulphur. Analysis:

	Calculated for $C_{14}H_{11}ON_3$.	Found.
N	17.72	17.79

The result agreed with that calculated for a diphenyloxytriazole. 1,5-Diphenyl-3-oxytriazole melts at 288°–290°. The

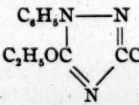
following synthesis proved, however, that our compound was the isomer or 1,3-diphenyl-5-oxytriazole.

Acetonephenylhydrazone and *benzoyl isocyanate* were slowly mixed in cold, dry benzene. Reaction took place at once, the solution was warmed for a few minutes and then, on cooling, a mass of crystals separated. On crystallizing several times from alcohol, colorless, microscopic, apparently hexagonal prisms were obtained. These melted, at about 139°–140°, to a clear, yellow oil which then turned red. A nitrogen determination agreed with that calculated for the semicarbazone, $C_6H_5CONHCON(C_6H_5).N : C(CH_3)_2$.

	Calculated for $C_{17}H_{17}O_2N_3$.	Found.
N	14.24	14.36

When this substance was warmed, for a few minutes, with dilute hydrochloric acid and then crystallized from alcohol fine, colorless needles were obtained, melting at 229°–230°. When these were mixed with the product of the hydrolysis of Wheeler and Dustin's compound, the melting-point was not altered. The two products were identical in every respect. 1,3-Diphenyl-5-oxytriazole is readily soluble in hot alcohol and only slightly soluble in boiling water, the solution having an acid reaction to litmus. It dissolves in ether and benzene.

1,3-Diphenyl-5-ethoxytriazole,

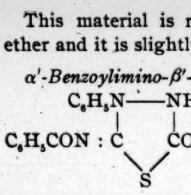


— Two grams of the above triazole and 0.6 gram of potassium hydroxide were dissolved in alcohol and an excess of ethyl bromide was added. The mixture was heated for 1 hour, at 100°. It was then evaporated and an oil was obtained which solidified when treated with water. On crystallizing from dilute alcohol shining, rhombic prisms separated, melting at 85°–86°. Analysis:

	Calculated for $C_{18}H_{15}ON_3$.	Found.
N	15.85	15.96

This material is readily soluble in alcohol, benzene and ether and it is slightly soluble in boiling water.

α'-Benzoylimino-β'-phenylthiobiazolon,



$C_6H_5CON : C \quad CO$.—The compound described by Wheeler

and Dustin, melting at 136°–138° (15 grams), was fused in an oil-bath, the temperature being kept at 140°–145° and hydrogen chloride was passed in for some time after the mass had solidified. The product was then extracted with hot, dilute alkali and filtered from unaltered material. It was precipitated with hydrochloric acid, washed and crystallized several times from alcohol, whereupon colorless needles were obtained melting, to a reddish-yellow oil, at 206°–207°. The yield was about 8 grams. Analysis:

	Calculated for $C_{15}H_{11}O_2N_2S$.	Found.
N	14.31	14.43

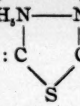
This material did not form an addition-product with ethyl iodide on standing in the cold. When boiled with strong alkali a portion was completely decomposed, the remainder being unaltered. It is slightly soluble in hot water, somewhat soluble in ether and benzene and readily soluble in boiling alcohol.

The *sodium salt* was not very readily soluble in cold alcohol. It was obtained by adding sodium ethylate to an alcoholic solution of the substance and it crystallized from alcohol in yellow needles, decomposing at about 240°.

The *silver salt* was prepared from the alcoholic solution of the sodium salt by adding the calculated quantity of silver nitrate, in dilute aqueous solution. It separated as a yellowish-white, amorphous precipitate, which was dried on a porous plate, then over sulphuric acid. Analysis:

	Calculated for $C_{15}H_{10}O_2N_2SAg$.	Found.
N	10.4	10.8

α-Ethoxy-α'-benzoylimino-β'-phenylbiazoline,



$C_6H_5CON : C \quad COC_6H_5$ (S).—The sodium salt described above does not react with ethyl bromide in the cold. α'-Benzoylimino-β'-phenylthiobiazolon (2 grams) was dissolved in the calculated amount of alcoholic sodium ethylate and heated with an excess of ethyl iodide, at 105°, for 2 hours. The contents of the tube were then evaporated and the residue, which consisted of unaltered biazolon and the ethoxy derivative, was purified by treating with alkali and crystallizing the insoluble material from alcohol. It then gave colorless or white prisms, melting at 137°–138° and, when mixed with the substance described by Wheeler and Dustin, the melting-point was not altered.

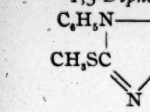
The same compound was formed when the silver salt of the biazolon was treated with ethyl iodide in the cold. When prepared by these methods the material is colorless. When obtained from benzoyl thiocyanate and ethyl phenylthioncarbazinate it is decidedly yellow at first and even upon repeated crystallization from alcohol it retains a yellowish tint. We also obtained this compound by the action of benzoyl isocyanchloride[1] on ethyl phenylthioncarbazinate, in chloroform.

In the previous paper it was stated that an alcoholic solution of silver nitrate desulphurizes this material. It now appears that the action was due to a decomposition. Some of the substance was boiled in alcohol with moist mercuric oxide, for 18 hours. It was not desulphurized and unaltered material was obtained when it was heated, for 4 hours, with the freshly prepared oxide, in benzene, at 140°–150°.

The following derivatives of 1,3-diphenyl-5-thiotriazole were prepared in order to further characterize the substance. The isomeric 1,5-diphenyl-3-thiotriazole and the corresponding derivatives have been described by Wheeler and Beardsley.[2]

[1] Johnson and Menge: THIS JOURNAL, **32**, 371 (1904).
[2] *Ibid.*, **27**, 257 (1902).

1,3-Diphenyl-5-methylmercaptotriazole,



—1,3-Diphenyl-5-thiotriazole was first obtained by Wheeler and Beardsley from formyl phenyl hydrazine and benzoyl thiocyanate. It is best prepared by the method described by Johnson and Menge.[1]

Molecular proportions of 1,3-diphenyl-5-thiotriazole and sodium ethylate, in alcoholic solution, were treated with an excess of methyl iodide and allowed to stand 12 hours. The alcohol was then evaporated and the oil thus obtained was washed with water. On cooling, it solidified and when crystallized from alcohol it gave large, colorless needles, melting at 56°–57°, to a clear liquid. It is readily soluble in ether and benzene, insoluble in cold and sparingly soluble in boiling water. It dissolves readily in hot alcohol. Analysis:

	Calculated for $C_{15}H_{12}N_3S$.	Found.
N	15.73	15.90

1,3-Diphenyl-5-ethylmercaptotriazole.—This was prepared by acting on the sodium salt of the thiotriazole with ethyl bromide, in alcoholic solution, as described above. It formed colorless, stout prisms from alcohol and melted at 52°–53°. Analysis:

	Calculated for $C_{16}H_{15}N_3S$.	Found.
N	14.95	15.06

When dissolved in hydrobromic acid it gave a salt melting at 152°. On boiling, the material reverts to 1,3-diphenyl-5-thiotriazole.

1,3-Diphenyltriazole-5-disulphide, $(C_{14}H_{10}N_3)_2S_2$.—The thiotriazole was dissolved in the calculated quantity of sodium hydroxide and a slight excess of iodine was added. The whole was then evaporated to dryness and the residue was extracted with benzene when fine, colorless needles were ob-

[1] THIS JOURNAL, 32, 369 (1904).

tained, melting at 182°–183°. The material was only slightly soluble in ether and alcohol and insoluble in water. Analysis:

	Calculated for $(C_{14}H_{10}N_2S)_2$.	Found.
N	16.67	16.76

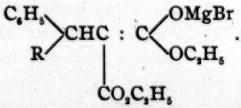
NEW HAVEN, CONN.,
March 3, 1905.

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

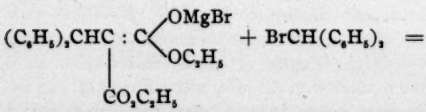
VI. REACTIONS WITH ETHYL BENZALMALONATE.

BY E. P. KOHLER.

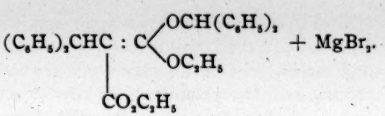
A number of recent investigations have shown that alkylidene malonic esters have an unusual capacity for combining with dissimilar atoms or groups.[1] It was to be expected, therefore, that the first reaction between ethyl benzalmalonate and Grignard's reagent would consist in direct addition. I have found that this is the case and that the structure of the product is represented by the formula:



This formula is based, mainly, on the reaction between the magnesium derivatives and diphenylbrommethane, which gives O-alkyl derivatives of substituted malonic esters. The product obtained with phenylmagnesium bromide, for example, reacts as follows:



[1] Ann. Chem. (Liebig), **218**, 143; Ber. d. chem. Ges., **26**, 1877; Ann. Chem. (Liebig), **239**, 338; THIS JOURNAL, **20**, 510; *Ibid.*, **31**, 243; Ann. Chem. (Liebig), **336**, 168.



It is difficult to introduce alkyl groups into substituted malonic esters that contain a branched chain and, occasionally, abnormal products are obtained in reactions with metallic derivatives of esters of this type; but, in the case under consideration, there is independent evidence that the magnesium compound has the same structure as the O-alkyl derivative. The latter, like the corresponding nitrile described in a previous paper, is an extremely unreactive substance—the carbethoxyl does not react with Grignard's reagent and it even resists saponification by the methods commonly used for this purpose. The inertness is evidently connected with its peculiar structure, since it is common to all the substances of this type that I have obtained.

The magnesium compound shows this same lack of activity, its carbethoxyl group is not attacked by organic magnesium compounds, although, as was shown by Valeur,[1] this reagent replaces both of the groups of malonic ester.

The reactions described in this paper can be used for preparing substituted malonic acids that are not easily made by other methods. The esters obtained by decomposing the magnesium compounds boil without decomposing and they are easily hydrolyzed to the corresponding acids, hence the yield of the latter is excellent. These reactions can also be used for preparing α,β-unsaturated acids, but in this case the yield is affected by the instability of some of the intermediate compounds.

EXPERIMENTAL.

The reaction between ethyl benzalmalonate and organic magnesium compounds is not affected by the relative amounts of the substances or the conditions under which they are brought together. This conclusion is based on the following preliminary experiments:

[1] Compt. rend., 132, 833.

Two solutions of methyl magnesium iodide, each containing 1 gram equivalent of magnesium, were made in the usual way and cooled in a freezing-mixture. An ethereal solution, containing half the calculated amount of ethyl benzalmalonate, was slowly added to the one, while the other was siphoned, drop by drop, into a similar solution containing twice the calculated amount of ester. After the liquids had remained in a freezing-mixture for several hours, portions of each were removed with a pipette and decomposed with ice-water. The remainders were boiled for 8 hours and then also poured into ice-water. The product was the same in all cases. The following procedure was, therefore, used in all subsequent experiments. An ethereal solution of the ester (1 mol.) was added, gradually, to a solution of the magnesium compound (1 mol.), cooled in ice-water. The resulting liquid was boiled for half an hour and then treated with the various reagents used. The magnesium derivative itself was not isolated.

Ethyl Diphenylmethylmalonate, $(C_6H_5)_2CHCH(CO_2C_2H_5)_2$.—The solution of the magnesium compound was poured into ice-water, the ethereal layer washed with water, dried with sodium sulphate and distilled under diminished pressure. The fraction boiling at 235°–250° (12 mm.) solidified in a freezing-mixture. After one crystallization from low-boiling ligroin the solid melted sharply at 63°. Analysis :

0.1540 gram substance gave 0.4248 gram CO_2 and 0.0963 gram H_2O.

	Calculated for $C_{20}H_{22}O_4$.	Found.
C	73.62	73.51
H	6.74	6.89

The ester separates from ligroin in fine needles. It is readily soluble in alcohol, ether, and carbon bisulphide ; moderately in low-boiling ligroin. The yield was excellent : 27 grams from 25 grams of ethyl benzalmalonate.

Sodium Ethyl Diphenylmethylmalonate,

$$(C_6H_5)_2CHC : C\begin{matrix}ONa\\OC_2H_5\end{matrix}$$
$$\quad\quad\quad

insoluble in alkalies and it gives no color reaction with ethereal solution of ferric chloride, but in ethereal solution it readily dissolves sodium, with evolution of hydrogen. The sodium derivative is soluble in ether, hence the surface of the metal remains clean and the action continues until the solution contains 1 atom of sodium per molecule of ester. The ether, on evaporation in a current of carefully dried air, deposits the sodium derivative in small, white needles. Analysis :

0.2112 gram substance gave 0.0428 gram Na_2SO_4.

	Calculated for $C_{20}H_{21}O_4Na$.	Found.
Na	6.61	6.55

Monoethyl Diphenylmethylmalonate, $(C_6H_5)_2CHCH\begin{matrix}CO_2C_2H_5\\CO_2H\end{matrix}$.—It is easy to hydrolyze ethyl diphenylmethylmalonate in steps. To get the ester acid an alcoholic solution of 1 molecule of ester and 1 of potassium hydroxide was allowed to remain, at the ordinary temperature, until the reaction was neutral to litmus. The solution was clear, but ether precipitated a potassium salt in fine, white needles. This was filtered, washed with ether and dissolved in water. On acidifying this solution the acid was precipitated as a crystalline solid. It was purified by recrystallization from alcohol. Analysis :

0.1511 gram substance gave 0.4005 gram CO_2 and 0.0857 gram H_2O.

	Calculated for $C_{18}H_{18}O_4$.	Found.
C	72.50	72.29
H	6.04	6.28

The acid is deposited in thick needles that melt at 165°–166° and give off carbon dioxide above 220°. It is readily soluble in ether and acetone, moderately in alcohol and sparingly in ligroin and in boiling water.

Diphenylmethylmalonic Acid, $(C_6H_5)_2CHCH_2(CO_2H)_2$.—Excess of strong, aqueous potassium hydroxide was added to an

alcoholic solution of the ester. The liquid became hot and in a short time a potassium salt began to separate in long, colorless needles. The salt was filtered and washed with absolute alcohol. From its aqueous solution hydrochloric acid precipitated an oil that soon solidified. The solid was purified by recrystallization from hot water. Analysis:

0.1926 gram substance gave 0.5022 gram CO_2 and 0.0915 gram H_2O.

	Calculated for $C_{18}H_{14}O_4$.	Found.
C	71.11	71.06
H	5.18	5.28

Diphenylmethylmalonic acid is readily soluble in alcohol and ether, moderately in hot water, very slightly in cold water. In boiling water it slowly loses carbon dioxide and passes into β,β-diphenylpropionic acid. It separates from water in thin plates and from alcohol in needles. It melts, with decomposition, at 190°–192°.

Ethyl Bromdiphenylmethylmalonate, $(C_6H_5)_2CHCBr(CO_2C_2H_5)_2$. — Bromine, that had been carefully dried by distillation from phosphorus pentoxide, was dropped into an ethereal solution of the magnesium derivative, obtained from 5 grams of magnesium, 34 grams of brombenzene and 32 grams of ethyl benzalmalonate. The reaction was so energetic that it was necessary to cool in a freezing-mixture. As soon as the color of bromine no longer disappeared on shaking, the mixture was poured into ice-water and the product isolated in the usual way. It was purified by crystallization from alcohol. Analysis:

0.1669 gram substance gave 0.3629 gram CO_2 and 0.0776 gram H_2O.

	Calculated for $C_{20}H_{21}O_4Br$.	Found.
C	59.26	59.19
H	5.15	5.16

The substance is readily soluble in acetone and ether, moderately in alcohol, sparingly in ligroin, From alcohol it separates in large, diamond-shaped plates, melting at 79°–80°.

Hydrolysis of Ethyl Bromdiphenylmethylmalonate.—I did not succeed in getting the dibasic acid. When an alcoholic solution of the ester and one equivalent of potassium hydroxide is kept in an ice chest, for several days, it usually deposits a mixture of potassium carbonate and the potassium salt of a brom-organic acid. The latter salt is extremely unstable, but it can be purified by dissolving it in the smallest possible quantity of water, at the ordinary temperature, adding a little alcohol and cooling this solution in ice-water. The pure salt forms a clear solution in ice-water. It separates from water in colorless needles. Analysis:

0.2346 gram substance gave 0.0535 gram K_2SO_4.

	Calculated for $C_{15}H_{12}O_2BrK.2H_2O$.	Found.
K	10.50	10.24

The analysis and the transformations described below show that this is potassium α-brom-β,β-diphenylpropionate formed according to the equation:

$$(C_6H_5)_2CHCBr(CO_2C_2H_5)_2 + 3KOH = (C_6H_5)_2CHCHBrCO_2K + 2C_2H_5OH + K_2CO_3.$$

At 130° the salt begins to lose water, but it also undergoes partial decomposition and the residue is no longer completely soluble in water. The same change takes place in water solution. Bromine ions can be detected in a dilute solution in ice-water a short time after it is made and, if such a solution be allowed to stand, it soon becomes turbid. The change, of course, takes place much more rapidly on warming. To determine the nature of the products a solution of 5 grams of the salt, in 100 grams of water, was boiled, for an hour, in a flask connected with an inverted condenser. The liquid was then cooled and extracted with ether. The ether, on evaporation, deposited 2.1 grams of a crystalline solid that melted at 124° and gave a bromine addition-product melting at 237°. This was stilbene. The aqueous solution, on evaporation, left potassium bromide, free from organic matter; the salt had, therefore, decomposed completely into stilbene, carbon dioxide and potassium bromide.

This remarkable change is essentially like that described by Elbs and Förster.[1] These investigators found that the polyhalogen derivatives of unsymmetrical diarylethanes regularly give stilbenes on reduction. On treating diphenyltrichlorethane, for example, with zinc dust and alcohol, they obtained stilbene itself:

$$(C_6H_5)_2CHCCl_3 \rightarrowtail C_6H_5CH{=}CHC_6H_5 + ZnCl_2.$$

In the case of potassium diphenylbrompropionate the result is evidently due to an ion reaction, since the change takes place in dilute aqueous solution and proceeds more rapidly in solutions of the sodium or potassium salts than in those of the free acid. It may be represented as follows:

$$(C_6H_5)_2CHCH\begin{cases}Br\\CO_2\end{cases} \rightarrowtail \overline{Br} + \left[(C_6H_5)_2CHCH\begin{cases}\\CO_2\end{cases}\right] \rightarrowtail$$

$$C_6H_5CH : CHC_6H_5 + CO_2.$$

It would be interesting to compare this result with some others that have been obtained by the action of bromine on aqueous solutions of salts; but as I am now studying this subject by kinetic methods I shall defer the discussion to a later paper.

The following experiment shows that, although potassium diphenylbrompropionate easily breaks down into simpler substances, it is, nevertheless, possible to eliminate hydrobromic acid and get β-phenylcinnamic acid without serious loss of material. Ten grams of the salt were added, in small quantities, to excess of potassium hydroxide in boiling, absolute alcohol. After boiling for an hour most of the alcohol was distilled, the residue poured into water and the milky solution extracted with ether. The ethereal solution, on evaporation, deposited less than 0.5 gram of stilbene, while the aqueous solution, when acidified, gave 4.55 grams of pure phenylcinnamic acid, melting at 158°, a yield of 80 per cent.

A fairly good yield of β-phenylcinnamic acid may also be obtained by adding ethyl bromdiphenylmethylmalonate, in small

[1] J. prakt. Chem., [2], 39, 45.

quantities, to strong, boiling, alcoholic potassium hydroxide; 22 grams of ester gave 8 grams of the unsaturated acid, a yield of 72 per cent.

α-Brom-β,β-diphenylpropionic Acid, $(C_6H_5)_2CHCHBrCO_2H$. —The pure acid was obtained by acidifying a solution of the pure potassium salt and recrystallizing the precipitate from a mixture of chloroform and ligroin. Analysis:

0.1342 gram substance gave 0.2920 gram CO_2 and 0.0480 gram H_2O.

	Calculated for $C_{15}H_{13}O_2Br$.	Found.
C	59.01	59.30
H	4.25	4.05

The acid is sparingly soluble in water; the solution changes much more slowly than those of its salts, but the acid ultimately decomposes completely into carbon dioxide, hydrobromic acid and stilbene.

Ethyl O-Acetyldiphenylmethylmalonate, $(C_6H_5)_2CHC(CO_2C_2H_5):C(OCOCH_3)(OC_2H_5)$. —In earlier papers it was shown that the reaction between acyl chlorides and the magnesium derivatives, formed by adding Grignard's reagent to unsaturated compounds, usually results in the replacement of the magnesium halide residue with an acyl group — the product being an O-acyl derivative. The magnesium compounds obtained from ethyl α-cyancinnamate, however, behave quite differently; the carbon chain is broken and the result is a magnesium derivative of a β-ketonic ester:

$$(C_6H_5)_2CHC(CN):C(OMgBr)(OC_2H_5) + CH_3COCl = (C_6H_5)_2CHCl + CH_3COC(CN):C(OMgBr)(OC_2H_5).$$

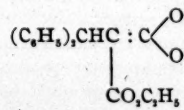
It was, therefore, of interest to ascertain whether the magnesium derivatives obtained from ethyl benzalmalonate would behave normally, or like those obtained from the corresponding nitrile. The former was found to be the case. Acetyl chloride, in slight excess, was added to the ethereal solution of the magnesium derivative, the mixture boiled for half an hour and poured into iced hydrochloric acid. The ethereal layer, on evaporation, deposited a crystalline solid and a small quantity of oil. The oil was drawn off with the pump, the crystals washed with a small quantity of cold ether and recrystallized from alcohol. Analysis:

0.1991 gram substance gave 0.5227 gram CO_2 and 0.1220 gram H_2O.

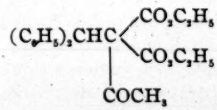
	Calculated for $C_{23}H_{24}O_5$.	Found.
C	71.74	71.65
H	6.52	6.69

The substance is readily soluble in chloroform, acetone and boiling alcohol; moderately in boiling ether; very slightly in low-boiling ligroin. It is deposited from alcohol in large, lustrous plates, melting at 92°.

It is extremely difficult to distinguish between the two possible formulas for this acetyl derivative:



I.



II.

Each of them represents a substance that would be incapable of forming metallic derivatives and indifferent to ferric chloride. A compound with the structure represented by I. would, on hydrolysis, necessarily give a substituted malonic acid; but some C-acyl derivatives of malonic ester are hydrolyzed in the same way. Phenacetylmalonic ester, for example, yields phenylacetic and malonic acids when saponified with bases. With dilute sulphuric acid its ester gives methyl benzyl ketone, but this method of hydrolysis has been applied

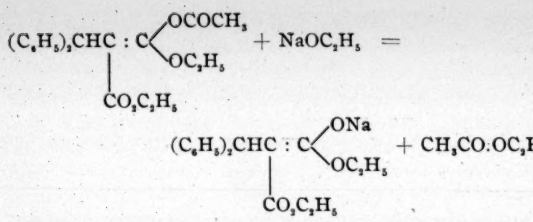
to so few esters of the kind that the result cannot be used as a basis for determining the structure of an unknown substance.

The acetyl derivative in question is hydrolyzed with the greatest ease. When it is allowed to stand, in alcoholic solution, with exactly one equivalent of sodium ethylate, the products are ethyl acetate and the same sodium derivative of ethyl diphenylmethylmalonate that is formed by the direct action of sodium on the ester. When the acetyl derivative is treated with one equivalent of alcoholic potassium hydroxide the principal products are potassium acetate and ethyl diphenylmethylmalonate, but the reaction always proceeds further, some of the ester being transformed into the ester salt previously described. With excess of boiling, alcoholic potassium hydroxide, the change into potassium acetate and potassium diphenylmethylmalonate is quantitative.

The most significant results are, probably, those obtained with Grignard's reagent. The acetyl derivative was added to an ethereal solution of phenyl magnesium bromide and the mixture boiled for several hours. The products, isolated in the usual way, were ethyl diphenylmethylmalonate and methyldiphenylcarbinol, melting at 98°. The reaction is represented by the following equation :

$$(C_6H_5)_2CHC(OCOCH_3)(OC_2H_5)CO_2C_2H_5 + 2C_6H_5MgBr = (C_6H_5)_2CHC(OMgBr)(OC_2H_5)CO_2C_2H_5 + (C_6H_5)_2C(CH_3)OMgBr.$$

It is hardly conceivable that such a reaction could take place with a compound that has the structure represented by II. I therefore regard the substance as an O-acetyl derivative. This is in harmony with its behavior towards sodium ethylate :

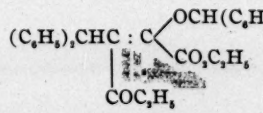


The oil that is formed along with the solid just described contains a second acetyl derivative. This could not be obtained in perfectly pure condition, because even the purest specimen did not solidify in a freezing-mixture and decomposed when distilled under greatly diminished pressure. The purest specimen was obtained as follows : An ethereal solution of the crude oil was washed with dilute sodium carbonate, dried over sodium sulphate and the ether evaporated in a current of dry air. The residue was repeatedly extracted with low-boiling ligroin, the first extract being discarded. The colorless oil, left after evaporating the ligroin, was heated at 150°, in a current of dry carbon dioxide, under 15 mm. pressure. The residue was analyzed :

0.1810 gram substance gave 0.4780 gram CO_2 and 0.1092 gram H_2O.

	Calculated for $C_{25}H_{24}O_5$.	Found.
C	71.74	72.00
H	6.52	6.70

The chemical properties of this substance are exactly the same as those of the solid acetyl derivative. It even gives the same products with phenylmagnesium bromide. It therefore seems to be a geometrical isomer of the solid, but I have not succeeded in transforming either of these substances into the other.



The magnesium derivatives obtained from ethyl benzalmalonate do not react with simple alkyl haloids. Ethereal solutions of several of these substances were boiled for hours with methyl iodide, isopropyl bromide, allyl iodide, tertiary butyl bromide and ethyl brommalonate, but in each case the alkyl haloid remained unchanged. With the unusually reactive diphenylbrommethane, however, a reaction takes place even at the ordinary temperature and the product is an O-alkyl derivative. Twelve grams of the haloid were added to an ethereal solution, obtained from 12 grams of ethyl benzalmalonate and the equivalent amount of phenylmagnesium bromide. The reaction started at once, the heat developed raising the temperature of the liquid to the boiling-point. The solution was boiled for 3 hours, then poured into ice-water. The ethereal layer, on evaporation, left a solid which was recrystallized from absolute alcohol. The substance was deposited in plates, melting at 132°. It is readily soluble in chloroform and acetone, moderately in alcohol and ether. Analysis:

I. 0.1797 gram substance gave 0.5297 gram CO_2 and 0.1050 gram H_2O.

II. 0.1623 gram substance gave 0.4822 gram CO_2 and 0.0941 gram H_2O.

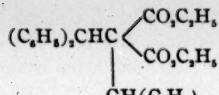
	Calculated for $C_{28}H_{28}O_4$.	Found. I.	II.
C	80.48	80.39	80.55
H	6.50	6.49	6.40

Molecular Weight Determined in Boiling Acetone.

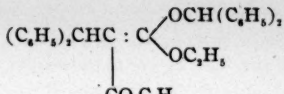
K = 1710.

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
52.00	0.6125	0.042	479
	1.1510	0.082	502
	1.9010	0.129	483
	Calculated for $C_{28}H_{28}O_4$,		492

It is easy to decide between the two possible formulas for this substance:



I.

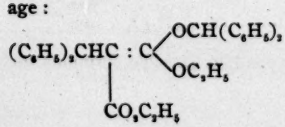


II.

If the substance were a C-alkyl derivative (I.) it should be easy to hydrolyze it to the corresponding acid or, at any rate, to transform it into an acid containing two diphenylmethyl groups. This is impossible. Boiling, alcoholic potassium hydroxide and boiling, dilute sulphuric acid (1 : 3) have no effect on the substance. It can be decomposed by heating at 150°–160° with alcoholic potassium hydroxide, but one of the diphenylmethyl groups is eliminated. The same result was obtained when the substance was heated, at 175°, with concentrated hydrochloric acid and the reaction was much cleaner, so that all the products could be isolated.

Twenty-five grams of the substance were sealed up with fuming hydrochloric acid and heated, at 175°–180°, for 8 hours. A considerable pressure in the tube was found to be due to carbon dioxide and ethyl chloride. The tube was emptied into water and the organic substances dissolved in ether. From the ethereal solution sodium carbonate extracted β,β-diphenylpropionic acid—the only organic acid found. The ethereal solution, left after extraction with sodium carbonate, was dried, the ether evaporated and the residue distilled. Almost the entire amount distilled at 210°, the boiling-point of diphenylmethylethyl ether. The boiling-point remained unchanged when the distillate was mixed with its own volume of this ether, made directly from diphenylbrommethane.

The original substance is evidently an O-alkyl derivative of ethyl diphenylmethylmalonate (II.). When heated with concentrated hydrochloric acid it breaks down at the double linkage :



$$(C_6H_5)_2CHCH_2CO_2H + CO_2 + C_2H_5OH + (C_6H_5)_2CHOC_2H_5.$$

Ethyl β-Phenylethylmalonate, $\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!CHCH(CO_2C_2H_5)_2$.—This compound was obtained by adding methylmagnesium iodide to ethyl benzalmalonate, decomposing the magnesium derivative with dilute acid and fractionating the product under diminished pressure. It is a colorless liquid that boils at 230°–235° (15 mm.). Analysis:

0.1442 gram substance gave 0.3590 gram CO_2 and 0.1001 gram H_2O.

	Calculated for $C_{15}H_{20}O_4$.	Found.
C	68.14	67.89
H	7.50	7.71

β-Phenylethylmalonic Acid, $\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!CHCH(CO_2H)_2$. — The potassium salt of the acid separated in needles when concentrated, aqueous potassium hydroxide was added to an alcoholic solution of the ester. The acid was recrystallized from hot water, which deposits it in large plates. Analysis:

0.1892 gram substance gave 0.4405 gram CO_2 and 0.1021 gram H_2O.

	Calculated for $C_{11}H_{12}O_4$.	Found.
C	63.46	63.49
H	5.80	5.98

Phenylethylmalonic acid is readily soluble in alcohol and ether, moderately in boiling water, sparingly in cold water and in ligroin. It melts at 144°. Above 170° it loses carbon dioxide rapidly. The colorless oil, left after heating several grams of the acid, at 180°, until there was no further gas evolution, solidified in the course of a week and could then be recrystallized from low-boiling ligroin. It was obtained in large, lustrous prisms, melting at 47°. Analysis:

0.1812 gram substance gave 0.4850 gram CO_2 and 0.1224 gram H_2O.

	Calculated for $C_{10}H_{12}O_2$.	Found.
C	73.11	72.94
H	7.30	7.51

The substance is evidently β-phenylbutyric acid. An acid of this composition and structure was described in a previous paper[1] as an oil. The specimen left over from the earlier experiments solidified completely when brought in contact with a crystal of the new preparation.

α-Brom-β,β-methylphenylbutyric Acid,

C_6H_5
CH_3 $>$ $CH_2CHCHBrCO_2H$.—This acid was made for the purpose of ascertaining whether substances of the type of bromdiphenylpropionic acid also undergo rearrangement into ethylene derivatives, when one of the hydrocarbon residues is aliphatic. One equivalent of ethyl benzalmalonate was added to an ethereal solution of ethylmagnesium bromide and the mixture boiled for an hour. The liquid was then cooled in a freezing-mixture and bromine added, drop by drop, until the color no longer disappeared on shaking. The mixture was poured into ice-water, the ethereal layer dried with sodium sulphate and the ether evaporated in a current of dry air. The pale-yellow oil that remained was cooled in a freezing-mixture and treated with a concentrated alcoholic solution of potassium hydroxide, containing a little less than one equivalent of the base. In the course of a few hours a potassium salt separated in long, silky needles. The salt gave no consistent analytical results and it could not be recrystallized from water or alcohol. From its solution in ice-water, hydrobromic acid precipitated a solid that could be purified by recrystallization from a mixture of chloroform and ligroin. Analysis:

0.2260 gram substance gave 0.4272 gram CO_2 and 0.0836 gram H_2O.

	Calculated for $C_{11}H_{13}O_2Br$.	Found.
C	51.32	51.54
H	4.40	4.18

[1] THIS JOURNAL, 33, 353.

α-Brom-β,β-methylphenylbutyric acid is readily soluble in alcohol, ether and chloroform, very slightly in water and ligroin. It melts at 176° and decomposes above 190°. A clear, aqueous solution of its potassium salt soon becomes milky, even at 0°. The aqueous solution of the acid is more stable, but it also becomes milky on standing.

An aqueous solution of the potassium salt was distilled with steam and the oily distillate extracted with ether. After drying the ethereal solution over calcium chloride, the ether was evaporated and the residue distilled. The temperature rose rapidly to 184° and the entire product passed over between 184° and 186°. A small quantity of the oil was treated with the calculated amount of bromine, dissolved in chloroform. The latter, on evaporation, left a solid which, after one recrystallization from ligroin, melted at 70°–71°. The oil is phenylbutylene, which boils at 186° and forms a bromine addition-product melting at 70°. It is evident, therefore, that the salts of this type decompose exactly like those of bromdiphenylpropionic acid:

$$\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>\!CHCHBrCO_2K = C_6H_5CH:CHC_2H_5 + KBr + CO_2.$$

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
March, 1905.

THE ACID OXALATES OF AMMONIUM.

BY P. T. WALDEN.

The work described in this paper was undertaken for the purpose of supplementing that of Foote and Andrew[1] on "The Acid Oxalates of Lithium, Sodium, Potassium and Caesium."

The experimental method used is that devised by Foote[2] and depends upon the principle that two simple salts with a common ion, when mixed in varying proportions and dissolved, will separate, at a fixed temperature, solid residues of a vary-

[1] THIS JOURNAL, **34**, 153.
[2] *Ibid.*, **30**, 330.

ing composition and leave solutions of a constant composition, except where a double salt forms. In this case the residue will be constant and the solution variable. The term salt is here used in the broad sense which includes all electrolytes, acid salts are, in this sense, double salts of hydrogen and metal.

The acid oxalates described in this paper are the only ones that can be prepared from mixtures of ammonium oxalate and oxalic acid, in water solution, at 25°. This statement is warranted by the experimental method employed and the principle which underlies it.

The compound, $(NH_4)_2C_2O_4.H_2C_2O_4.2H_2O$, described by Rammelsberg,[1] I have been unable to prepare, but I have obtained both the acid salts which Nichols[2] describes,

$$(NH_4)_1C_2O_4.3H_2C_2O_4.4H_2O \text{ and } (NH_4)_1C_2O_4.H_2C_2O_4.H_2O.$$

It is interesting to notice that in Ladenburg's "Handwörterbuch der Chemie" (1890) and in Beilstein (1893) Rammelsberg's formula for the 1 : 1 salt is retained, while Roscoe and Schorlemmer (1884) give only Nichols' formula for this salt.

In carrying out each experiment enough of the mixture of ammonium oxalate and oxalic acid was dissolved, in about 15 cc. of hot water, to make a solution that would crystallize when cooled. This was put in a thermostat, kept at 25° and constantly shaken for at least 48 hours. Samples of the solid residue and of the solution were then taken out and analyzed for ammonium oxalate and for oxalic acid. Twenty different mixtures were prepared and examined before it was evident that all the essential conditions had been covered. The proportion of salt to acid varied from almost pure ammonium oxalate at one end to almost pure oxalic acid at the other.

The samples for analysis were boiled with potassium hydroxide to expel ammonia, which was absorbed in standard hydrochloric acid solution and this was then titrated with standard ammonium hydroxide. Total oxalate was deter-

[1] Pogg. Ann., 93, 24 (1854).
[2] Chem. News, 22, 14 (1870).

mined by titration with permanganate and the per cent of free oxalic acid calculated from these values.

The analytical results for solutions and residues are shown below. Italics indicate analyses of pure acid salts :

	Per cent of $(NH_4)_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in solution.	Per cent of $(NH_4)_2C_2O_4$ in residue.	Per cent of $H_2C_2O_4$ in residue.
1	0.22	10.30	6.12	68.05
2	0.35	10.00	12.39	64.96
3	0.28	10.30	25.32	57.68
4	0.46	7.24	*26.32*	*57.57*
5	2.44	2.59	*26.58*	*57.72*
6	3.65	2.80	*26.82*	*57.67*
7	4.99	3.41	*27.03*	*57.51*
8	5.20	3.64	31.90	54.08
9	5.25	3.49	41.55	47.12
10	5.24	3.51	48.36	41.83
11	5.04	3.61	52.48	39.44
12	5.36	3.38	*53.37*	*38.53*
13	6.27	3.04	*53.18*	*37.71*
14	7.03	2.90	*53.26*	*38.94*
15	7.22	2.90	57.18	33.95
16	7.12	2.89	70.95	18.25
17	7.15	2.88	74.55	14.80
18	7.17	2.73	75.55	13.14
19	6.91	2.11	77.38	11.10
20	6.92	2.31	86.62	0.00
Calculated for $(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$			26.61	57.94
Calculated for $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$			53.45	38.79

It will be seen, from the above table, that mixtures 4, 5, 6 and 7, on the one hand and 12, 13 and 14, on the other, crystallized out solids, at 25°, which were found to be almost constant in composition, while the solutions from which they came showed a steadily varying proportion of components. Evidently, then, we have only two acid ammonium oxalates capable of existence at this temperature, *viz.* :

$(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$ and $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$.

The theoretical composition of these salts, as it is given below

the table, is seen to agree, approximately, with the results obtained by analyzing the solid residues from those solutions the composition of which varied (4, 5, 6 and 7 and 12, 13, and 14).

The same result is shown, graphically, in Fig. I., where the percentages of oxalic acid in solution are plotted as ordinate and those in the residue as abscissa.

Because of the very slight variation in the composition of the solutions from which the salt $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$ forms, it was thought that conditions might be found, by changing the temperature, where this salt would decompose into ammonium oxalate and the 3 : 1 acid salt, according to the equation:

$$3(NH_4)_2C_2O_4.H_2C_2O_4.H_2O + 3H_2O = 2(NH_4)_2C_2O_4.H_2O + (NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O.$$

Such a change would make itself evident by an irregular change of volume at the inversion temperature and this temperature can readily be found by the use of a dilatometer.[1]

Accordingly, some of this salt was prepared, mixed with a little ammonium oxalate, moistened with its mother-liquor and placed in a dilatometer, which was then filled with toluene to register the change of volume. This was subjected to a gradual rise of temperature, between its cryohydric temperature (about —4°) at one end and 70° at the other. A gradual and regular change of volume only was observed. It was, therefore, concluded that the 1 : 1 salt is stable through this range of temperature conditions and the attempt to decompose it was abandoned.

By a simple calculation from the table of solubilities, given above, we can ascertain whether or not the acid oxalates here described can be recrystallized from water. Evidently, if a double or acid salt can be recrystallized from water, it should be capable of forming from a solution containing the same relative quantities of the constituent simple salts present in the double one.

$(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$ contains 26.61 parts of $(NH_4)_2C_2O_4$: 57.94 parts of $H_2C_2O_4$.

[1] Van 't Hoff: "Vorles. über Bild. u. spalt. von. Doppelsalzen."

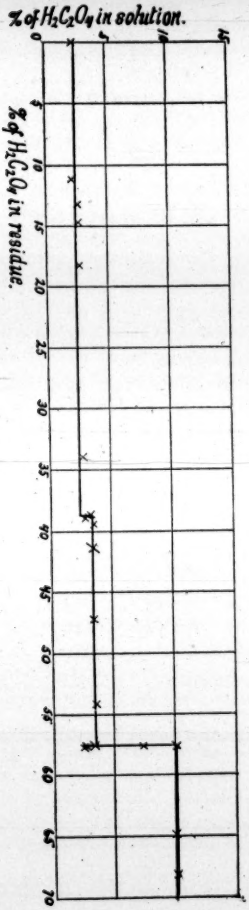

% of $H_2C_2O_4$ in solution.
% of $H_2C_2O_4$ in residue.
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70

Fig. 1.

We find, from the table, that the solutions from which this salt was obtained consist of 46 parts of $(NH_4)_2C_2O_4$: 724 parts of $H_2C_2O_4$ in solution 4 and 499 parts of $(NH_4)_2C_2O_4$: 341 parts of $H_2C_2O_4$ in solution 7.

Calculating these proportions to correspond to the percentages of the acid salt above, we have: 26.61 parts of $(NH_4)_2C_2O_4$: 418.80 parts of $H_2C_2O_4$ in solution 4 and 26.61 parts of $(NH_4)_2C_2O_4$: 18.19 parts of $H_2C_2O_4$ in solution 7.

It will be seen that the composition of the acid salt falls within these limits and, therefore, it can be recrystallized from water.

Calculating, in the same way, for the salt $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$ we find the composition of the solutions from which it forms to be 53.45 parts of $(NH_4)_2C_2O_4$: 33.70 parts of $H_2C_2O_4$ in solution 12 and 53.45 parts of $(NH_4)_2C_2O_4$: 22.05 parts of $H_2C_2O_4$ in solution 14.

The composition of the 1 : 1 acid salt is 53.45 parts of $(NH_4)_2C_2O_4$: 38.79 parts of $H_2C_2O_4$. Therefore this salt is not susceptible of recrystallization.

An experimental verification of this point was made by preparing crops of the two acid salts, crystallizing them from water at 25° and analyzing the substances obtained. The results are given below:

	Calculated for $(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$.	Found for salt made from simple salts. A.	Found for salt made from simple salts. B.	Found for recrystallized salt. A.	Found for recrystallized salt. B.
$(NH_4)_2C_2O_4$	26.61	27.24	27.21	26.33	. .
$H_2C_2O_4$	57.94	57.49	57.57	58.11	58.04
H_2O	15.45	. .	. .	. .	. .

	Calculated for $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$.	Found for salt made from simple salts. A.	Found for salt made from simple salts. B.	Found for recrystallized salt. A.
$(NH_4)_2C_2O_4$	53.45	52.95	53.01	25.60
$H_2C_2O_4$	38.79	38.85	38.94	56.53
H_2O	7.76	. .	. .	. .

SHEFFIELD LABORATORY,
YALE UNIVERSITY,
NEW HAVEN, CONN.,
March, 1905.

THE ACID OXALATES OF LITHIUM, SODIUM, POTASSIUM AND CAESIUM AND THEIR SOLUBILITY.

By H. W. Foote and I. A. Andrew.

The acid oxalates of lithium, sodium, potassium and caesium have been investigated by the same method used by Walden in the preceding article, the object being to determine all the stable acid salts capable of forming at 25° and the solubility conditions under which they form. The method depends on the principle that, when the components of the acid salts are mixed in varying proportions and treated with water at a constant temperature, the residue remains constant in composition and the solution varies if a pure acid oxalate is present, while, on the other hand, the residue varies and the solution remains constant in composition when a mixture of two oxalates is present. The mixtures were prepared and treated as in the preceding article. Both solutions and residues were analyzed. In the analysis, oxalic acid was determined by titrating with standard sodium hydroxide and total oxalate by titration with potassium permanganate. The amount of alkali oxalate could then be calculated.

The tabulated results which follow are divided into groups, each group representing either (1) constant solubility and varying residue, corresponding to a mixture of salts, or (2) varying solubility and constant residue corresponding to a pure double salt. The residues which are constant, showing pure double salt, are italicized. The solubility of oxalic acid and of the alkali oxalates alone is also given. All the results are for 25°.

1. *Oxalic Acid and Lithium Oxalate.*

Rammelsberg[1] described the salt $HLiC_2O_4.H_2O$, which was afterwards obtained by Souchay and Lenssen[2] and by Troost.[3] We find but this one salt. The results are given in Table I.:

[1] Ann. Chem. (Liebig), 56, 221.
[2] *Ibid.*, 100, 308.
[3] Ann. Chim. Phys., [3], 51, 103.

Table I.—Solubility of Lithium Oxalate and Oxalic Acid at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Li_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Li_2C_2O_4$ in residue.	Residue contains:
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.66	2.96	68.08	1.10	$H_2C_2O_4.H_2O$ and
3	10.54	3.11	47.20	33.38	$HLiC_2O_4.H_2O$
4	8.08	3.18	*39.21*	*44.77*	$HLiC_2O_4.H_2O$
5	2.60	5.03	*39.22*	*44.59*	
6	2.16	6.54	24.33	66.23	$HLiC_2O_4.H_2O$
7	2.12	6.61	2.84	94.68	and $Li_2C_2O_4$
8	none	5.87			$Li_2C_2O_4$
Cal. for $HLiC_2O_4.H_2O$			39.46	44.74	

2. Oxalic Acid and Sodium Oxalate.

Graham[1] described the compound $HNaC_2O_4.H_2O$, which has been prepared, repeatedly, by others since then. We have found but this one salt. The results are given in Table II. :

Table II.—Solubility of Oxalic Acid and Sodium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Na_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Na_2C_2O_4$ in residue.	Residue contains:
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.48	0.82	68.35	4.35	$H_2C_2O_4.2H_2O$ and
3	10.52	0.87	63.22	11.18	$HNaC_2O_4.H_2O$
4	10.50	0.82	50.26	29.67	
5	9.15	0.71	*35.15*	*52.50*	
6	6.88	0.86	*34.49*	*51.19*	$HNaC_2O_4.H_2O$
7	1.14	1.25	*34.63*	*51.84*	
8	0.47	3.20	*34.50*	*51.66*	
9	0.42	3.84	27.30	62.67	$HNaC_2O_4.H_2O$
10	0.43	3.86	3.27	95.79	and $Na_2C_2O_4$
11	none	3.60			$Na_2C_2O_4$
Cal. for $HNaC_2O_4.H_2O$			34.60	51.55	

3. Oxalic Acid and Potassium Oxalate.

There are two well-known acid potassium oxalates,

$$H_3K(C_2O_4)_2.2H_2O \quad \text{and} \quad HKC_2O_4.$$

[1] Ann. Chem. Liebig, **29**, 1.

The latter salt, according to Wyrouboff,[1] is anhydrous above 15° and contains water of crystallization below that temperature. There appears to be some doubt as to the amount of water of crystallization present in this salt. Nichols[2] gives the formula $2H_2K_2(C_2O_4)_2.H_2O$, which agrees with Rammelsberg,[3] while Wyrouboff assigns the formula $HKC_2O_4.H_2O$, which agrees with Graham.[4] At 25° we obtained the anhydrous salt. We have also found a third salt, $H_2C_2O_4.2K_2C_2O_4.2H_2O$, which does not appear in the literature. This salt forms only under a narrow range of conditions and does not recrystallize, which probably accounts for its not having been described previously. The results obtained are in Table III.:

Table III.—Solubility of Oxalic Acid and Potassium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $K_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $K_2C_2O_4$ in residue.	Residue contains:
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.30	0.03	68.67	6.34	$H_2C_2O_4.2H_2O$
3	10.30	0.08	58.44	22.68	and
4	10.34	0.02	53.66	32.58	$H_3K(C_2O_4)_2.2H_2O$
5	9.26	0.13	*53.04*	*32.66*	$H_3K(C_2O_4)_2.2H_2O$
6	3.39	0.63	*53.00*	*33.54*	
7	2.05	4.23	51.10	36.13	$H_3K(C_2O_4)_2.2H_2O$
8	2.08	4.27	38.96	59.66	and
9	2.05	4.33	34.94	65.10	HKC_2O_4
10	1.16	11.50	*34.81*	*64.80*	HKC_2O_4
11	0.99	16.93	*34.98*	*65.49*	
12	0.85	21.06	34.89	65.52	HKC_2O_4 and
13	0.86	21.12	22.22	71.37	$H_3K_4(C_2O_4)_3.2H_2O$
14	0.82	21.49	*19.50*	*73.60*	
15	0.64	23.52	*19.65*	*73.58*	$H_3K_4(C_2O_4)_3.2H_2O$
16	0.57	24.88	*19.51*	*73.61*	
17	0.42	27.52	17.56	74.47	$H_3K_4(C_2O_4)_3.2H_2O$
18	0.45	27.52	3.50	86.68	and $K_2C_2O_4.H_2O$
19	none	27.40			$K_2C_2O_4.H_2O$

[1] Centrabl., **2**, 843 (1900).
[2] Chem. News, **22**, 14.
[3] Pogg. Ann., **93**, 24.
[4] Ann. Chem. (Liebig), **29**, 1.

Below is given the theoretical composition of the three acid salts, with the average results obtained by analysis. Water was found by difference :

	Per cent $H_2C_2O_4$.	Per cent $K_2C_2O_4$.	Per cent H_2O.
$H_3K(C_2O_4)_2.2H_2O$ (theory)	53.12	32.70	14.18
" (found)	53.02	33.10	13.88
HKC_2O_4 (theory)	35.12	64.88	. .
" (found)	34.90	65.15	. .
$H_2K_4(C_2O_4)_3.2H_2O$ (theory)	19.63	72.51	7.86
" (found)	19.55	73.60	6.85

4. Oxalic Acid and Caesium Oxalate.

No oxalate of caesium appears to have been described. Caesium oxalate was made by neutralizing caesium carbonate with oxalic acid and evaporating to crystallization. Analysis, by titrating with potassium permanganate, gave :

	Calculated for $Cs_2C_2O_4.H_2O$.	Found.
$Cs_2C_2O_4$	95.16	95.26
H_2O (by diff.)	4.84	4.74

The salt has, therefore, the composition $Cs_2C_2O_4.H_2O$. Its solubility in water, at 25°, is very great, the solution containing 75.82 per cent of anhydrous salt.

The solubility of the mixtures of caesium oxalate and oxalic acid is given in Table IV. :

Table IV.—Solubility of Oxalic Acid and Caesium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Cs_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Cs_2C_2O_4$ in residue.	Residue contains :
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.29	0.73	67.20	6.90	$H_2C_2O_4.2H_2O$
3	10.34	0.46	45.85	40.70	and
4	10.26	0.64	42.00	46.07	$H_3Cs(C_2O_4)_2.2H_2O$
5	7.90	9.92	*38.45*	*51.44*	
6	3.93	23.03	*38.18*	*52.07*	$H_3Cs(C_2O_4)_2.2H_2O$
7	4.11	25.12	*38.53*	*51.28*	
8	4.25	27.55	38.01	51.99	$H_3Cs(C_2O_4)_2.2H_2O$
9	4.59	27.59	34.59	. .	and
10	4.21	27.51	33.81	64.60	$H_4Cs_2(C_2O_4)_3$.

Table IV. (Continued).—Solubility of Oxalic Acid and Caesium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Cs_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Cs_2C_2O_4$ in residue.	Residue contains:
11	4.27	28.30	*32.87*	*66.06*	
12	4.33	32.26	*32.27*	*68.10*	$H_4Cs_2(C_2O_4)_3$
13	4.40	35.90	*32.20*	*67.55*	
14	4.83	40.10	27.71	69.99	$H_4Cs_2(C_2O_4)_3$
15	4.83	39.82	27.91	72.01	and
16	4.79	40.37	23.92	78.92	$HCsC_2O_4$
17	4.45	42.32	*20.50*	*79.92*	
18	3.56	42.44	*20.14*	*79.54*	
19	3.62	47.92	*20.36*	*80.84*	$HCsC_2O_4$
20	3.05	48.80	*19.93*	*80.45*	
21	1.79	60.46	*20.49*	*81.58*	
22	1.04	68.69	*19.02*	*82.17*	
23	0.92	71.48	18.39	80.44	$HCsC_2O_4$
24	0.92	70.97	16.68	. .	and
25	0.87	71.44	16.32	83.08	$H_6Cs_6(C_2O_4)_7$
26	0.77	73.45	*15.87*	*83.83*	
27	0.76	73.84	*16.01*	. .	$H_6Cs_6(C_2O_4)_7$
28	0.80	74.04	*15.80*	*83.59*	
29	0.75	74.04	*15.88*	. .	
30	0.75	75.26	7.94	87.71	$H_6Cs_6(C_2O_4)_7$
31	0.73	75.14	4.32	90.74	and
32	0.76	75.22	3.84	89.64	$Cs_2C_2O_4.H_2O$
33	none	75.82			$Cs_2C_2O_4.H_2O$

In the results, the four italicized groups have a nearly constant residue while the solution varies, so that pure double salts are evidently present. It was not easy to obtain the residues in pure condition toward the caesium end, on account of the very great excess of caesium oxalate in the solution, which was also somewhat syrupy.

The average results obtained for the acid salts, together with the calculated values, are as follows:

	$H_2C_2O_4$.	$Cs_2C_2O_4$.	H_2O.
$H_3Cs(C_2O_4)_2.2H_2O$ (calculated)	38.81	50.84	10.35
" (found)	38.39	51.60	10.00
$H_4Cs_2(C_2O_4)_3$ (calculated)	33.73	66.27	. .
" (found)	32.45	67.24	. .
$HCsC_2O_4$ (calculated)	20.28	79.72	. .
" (found)	20.07	80.42	. .
$H_6Cs_2(C_2O_4)_7$ (calculated)	16.03	83.97	. .
" (found)	15.89	83.71	. .

The last salt is somewhat complicated in composition, but it is believed the formula given is the correct one. If it were the 1 : 2, corresponding to the new potassium salt, it would contain 11.28 per cent of oxalic acid. As it is removed from a solution containing a large excess of caesium oxalate, however, the residue analyzed would tend to have less oxalic acid and more caesium oxalate than is required by the theory instead of the reverse, which would be the case if the salt were the 1 : 2.

Comparison of the Solubilities of the Acid Alkali Oxalates.

For the sake of comparison, the solubility results shown in the previous tables, together with those of Walden on the acid ammonium oxalates, have been recalculated to show the molecules of oxalic acid and of alkali oxalate dissolved by 100 molecules of water. In recalculating, the average solubility results were used where a mixture of two salts was present. These results are given in the following tables, the numbers in the first column referring to the corresponding results in the preceding tables, where the percentage composition of the solutions was given :

Table V.—Oxalic Acid and Lithium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $Li_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.457	0.622
3	"	"
4	1.823	0.633
5	0.563	0.962
6	0.469	1.273
7	"	"
8	none	1.101

Table VI.—Oxalic Acid and Sodium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $Na_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.370	0.130
3	"	"
4	"	"
5	2.032	0.106
6	1.493	0.125
7	0.234	0.172
8	0.098	0.446
9	0.090	0.541
10	"	"
11	none	0.502

Table VII.—Oxalic Acid and Ammonium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $(NH_4)_2C_2O_4$ to 100 molecules H_2O.
1	2.281	0.045
2	"	"
3	"	"
4	1.570	0.072
5	0.546	0.373
6	0.599	0.566
7	0.745	0.791
8	0.781	0.824
9	"	"
10	"	"
11	"	"
12	0.741	0.853
13	0.671	1.00
14	0.645	1.13
15	0.599	1.14
16	"	"
17	"	"
18	"	"
19	"	"
20	none	0.775

Table VIII.—Oxalic Acid and Potassium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $K_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.302	0.005
3	"	"
4	"	"
5	2.046	0.016
6	0.707	0.071
7	0.440	0.495
8	"	"
9	"	"
10	0.266	1.427
11	0.240	2.235
12	0.221	2.928
13	"	"
14	0.211	2.998
15	0.169	3.361
16	0.153	3.617
17	0.122	4.14
18	"	"
19	none	4.09

Table IX.—Oxalic Acid and Caesium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $Cs_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.314	0.035
3	"	"
4	"	"
5	1.924	0.614
6	1.077	1.61
7	1.162	1.81
8	1.279	2.06
9	"	"
10	"	"
11	1.267	2.14
12	1.367	2.59
13	1.476	3.07
14	1.752	3.71
15	"	"
16	"	"
17	1.673	4.05

Table IX. (Continued).—Oxalic Acid and Caesium Oxalate.

	Molecules $C_2H_2O_4$ to 100 molecules H_2O.	Molecules $Cs_2C_2O_4$ to 100 molecules H_2O.
18	1.320	4.00
19	1.495	5.04
20	1.268	5.16
21	0.949	8.16
22	0.688	11.56
23	0.648	13.06
24	"	"
25	"	"
26	0.598	14.51
27	0.599	14.81
28	0.636	14.99
29	0.596	14.96
30	0.625	15.93
31	"	"
32	"	"
33	none	15.97

The above results (Tables V.–IX.) are shown in the diagram, where the molecules of oxalic acid are plotted as ordinate and the molecules of alkali oxalate as abscissa. The results for caesium oxalates are not plotted beyond the point corresponding to a mixture of $H_4Cs_2(C_2O_4)_3$, and $HCsC_2O_4$, as they would run beyond the limits of the diagram. A, on the ordinate, represents the solubility of pure oxalic acid and from this point run dotted lines—some of them very short—showing the solubility of oxalic acid in solutions containing small quantities of the alkali oxalates. The solubility of each alkali oxalate alone is represented by a point on the abscissa and the dotted lines show the varying solubility of each oxalate in the presence of small amounts of oxalic acid in solution. The form of these curves was not determined by experiment, so they are represented as straight lines. The dotted lines running from A end in points representing the solubility of oxalic acid with an acid salt, while the dotted lines running from the abscissa end in points showing the solubility of each alkali oxalate in the presence of an acid salt. From the points where the dotted lines end, the curves represent the solubility of a pure

A
B
C
D
E
F
Na
Li
Cs
NH4
K
1:1
2:1
3:1
1:2
3:4
H2C2O4
M2C2O4
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0.5
1.0
1.5
2.0
2.5
3.0

acid salt. In the case of lithium and of sodium there is but one curve, as but one acid salt forms. With ammonium, potassium and caesium, which form more than one acid salt, the curves consist of two or more parts, representing the varying solubility of each salt. The points where two salts are present together are represented on the curves by circles and are the points where the different parts of the curve intersect. The salt is indicated which is present along each curve.

In comparing the curves, it will be noted that the oxalates of sodium, lithium and ammonium show very limited solubility and, of these three, ammonium forms one more salt than the other two, which agrees with the general observation that ammonium has more tendency to form double salts than sodium or lithium. On the other hand, comparing the oxalates of ammonium, potassium and caesium, all with a pronounced tendency toward double salt formation, it will be noted that the number of acid salts increases with the solubility of the single oxalates. Judging from the solubility curves, the reason that ammonium oxalate does not form as many acid salts as potassium oxalate is that their formation, toward the ammonium end, is excluded by the limited solubility of ammonium oxalate.

Whether a salt can be recrystallized or not, at 25°, can readily be determined from the diagram.[1] For instance, suppose it is to be determined whether the salt $HLiC_2O_4.H_2O$ can be recrystallized or not. If the salt is dissolved in water it will form a solution containing equal molecules of lithium oxalate and oxalic acid and the composition of the solution will be represented by some point on the line OD. This line cuts the curve of solubility of the salt $HLiC_2O_4.H_2O$, showing that this salt can be in equilibrium with solutions containing an eqnal number of molecules of lithium oxalate and oxalic acid. The salt can, therefore, be recrystallized. On the other hand, the line OD just fails to intersect the curve of solubility for the double salt $HNH_4C_2O_4.\frac{1}{2}H_2O$, but intersects, instead, the curve for the salt $H_3NH_4(C_2O_4)_2.2H_2O$. On recrystallizing, therefore, the 1 : 1 salt would, at first, yield the 3 : 1, followed by a mixture of the 3 : 1 and 1 : 1.

[1] Van 't Hoff: "Vorles. über Bild. u. Spaltung von Doppelsalzen."

The lines OB, OC, OD, OE and OF represent solutions of the salts $H_3M(C_2O_4)_2$, $H_4M_2(C_2O_4)_3$, HMC_2O_4, $H_8M_3(C_2O_4)$, and $H_2M_4(C_2O_4)_3$, respectively, where M represents an alkali metal or ammonium. By noting the intersections of these lines with the curves for the acid salts, the conduct of each salt, on recrystallizing at 25°, can be given.

3 : 1 Salts.—The line OB cuts the curves of solubility of the salts $H_3Cs(C_2O_4)_2.2H_2O$, $H_3NH_4(C_2O_4)_2.2H_2O$ and $H_3K(C_2O_4)_2.2H_2O$. These salts can be recrystallized.

2 : 1 Salts.—Only $H_4Cs_2(C_2O_4)_3$ is known. The line OC, corresponding to solutions of this salt, cuts the curve of solubility of the 3 : 1 salt. On recrystallizing, the 2 : 1 yields the 3 : 1.

1 : 1 Salts.—The line OD cuts the solubility curves of the 1 : 1 salts for lithium and sodium. These salts recrystallize. It cuts the solubility curves of the 3 : 1 salts for caesium, ammonium and potassium. The 1 : 1 salts of these metals, therefore, yield the 3 : 1 salt when first recrystallized. The line comes so near the point of intersection of the curves for the 1 : 1 and 3 : 1 salts for potassium and ammonium, however, that after a small amount of the 3 : 1 salt had formed a mixture of the 3 : 1 and 1 : 1 would separate.

3 : 4 Salts.—Only the caesium salt of this type forms. It yields the 3 : 1 on recrystallizing.

1 : 2 Salts.—Only the potassium salt forms. It yields the 1 : 1 salt on recrystallizing.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
March, 1905.

ON CERTAIN ALLEGED DOUBLE OXALATES.

BY H. W. FOOTE AND I. A. ANDREW.

The following double alkali oxalates are mentioned in the literature :

$KNaC_2O_4$,[1] $NH_4KC_2O_4$,[2] $NH_4LiC_2O_4$.[3]

Although the formation of these double oxalates has been

[1] Wenzel, mentioned by Rammelsberg : Pogg. Ann., 79, 562.
[2] Wenzel, mentioned by Souchay and Lenssen : Ann. Chem. (Liebig), 99, 31.
[3] Ladenburg : Handwörterb. der Chemie, 8, 398.

doubted,[1] it seemed worth while to test for them by the solubility method, used in the two preceding articles. Two mixtures were prepared in each case, each containing an excess of one oxalate or the other and the solubility was determined at 25°.

In the mixtures of sodium and potassium oxalates, potassium was determined as potassium platinic chloride and total oxalate by titration with permanganate, from which the amount of each oxalate was calculated. Where ammonium and potassium oxalates or ammonium and lithium oxalates were present, ammonium was determined by distilling from sodium hydroxide into standard acid and total oxalate by titrating with permanganate.

The following results were obtained :

Table I.—Solubility of Sodium and Potassium Oxalates at 25°.

	$K_2C_2O_4$ in solution.	$Na_2C_2O_4$ in solution.	$K_2C_2O_4$ in residue.	$Na_2C_2O_4$ in residue.	Residue contains.
1	27.40	none			$K_2C_2O_4.H_2O$
2	26.22	2.37	83.58	6.94	$K_2C_2O_4.H_2O$ and
3	26.09	2.51	7.60	89.46	$Na_2C_2O_4$
4	none	3.60			$Na_2C_2O_4$

Table II.—Solubility of Ammonium and Potassium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	$K_2C_2O_4$ in solution.	$(NH_4)_2C_2O_4$ in residue.	$K_2C_2O_4$ in residue.	Residue contains :
1	none	27.40			$K_2C_2O_4.H_2O$
2	2.80	25.94	6.14	84.24	$K_2C_2O_4.H_2O$ and
3	2.78	25.98	75.68	13.07	$(NH_4)_2C_2O_4.H_2O$
4	5.07	none			$(NH_4)_2C_2O_4.H_2O$

Table III.—Solubility of Ammonium and Lithium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	$Li_2C_2O_4$ in solution.	$(NH_4)_2C_2O_4$ in residue.	$Li_2C_2O_4$ in residue.	Residue contains :
1	none	5.87	5.71	94.75	$Li_2C_2O_4$
2	4.80	5.75	5.71	94.75	$Li_2C_2O_4$ and
3	4.80	5.76	82.40	5.75	$(NH_4)_2C_2O_4.H_2O$
4	5.07	none			$(NH_4)_2C_2O_4.H_2O$

[1] Rammelsberg : *Loc. cit.* ; Souchay and Lenssen : *Loc. cit.*

In the above results it will be noticed that the solubility of the two mixtures in each table was practically constant, though the residues were so different in composition. This could be true only in case the same salts were present in the residue. Had a double salt formed, the two solubility results would have been different. We therefore conclude that the three double oxalates, mentioned at the beginning of the article, do not exist at 25°.

The results obtained agree with the observations of Rammelsberg and of Souchay and Lenssen, though the method used was different.

A large number of double oxalates of ammonium with magnesium, zinc and cadmium have been described and are tabulated in the following list:

Ammonium magnesium oxalates.

$7(NH_4)_2C_2O_4.MgC_2O_4.8H_2O$,[1]
$6(NH_4)_2C_2O_4.MgC_2O_4.10H_2O$,[2]
$6(NH_4)_2C_2O_4.MgC_2O_4.9H_2O$,[1]
$5(NH_4)_2C_2O_4.MgC_2O_4.8H_2O$,[1]
$13(NH_4)_2C_2O_4.5MgC_2O_4.24H_2O$,[1]
$(NH_4)_2C_2O_4.3MgC_2O_4.2H_2O$.[3]

Ammonium zinc oxalates.

$2(NH_4)_2C_2O_4.ZnC_2O_4.3H_2O$,[2]
$(NH_4)_2C_2O_4.ZnC_2O_4.3H_2O$.[4]

Ammonium cadmium oxalates.

$8(NH_4)_2C_2O_4.CdC_2O_4.11H_2O$,[5]
$6(NH_4)_2C_2O_4.CdC_2O_4.9H_2O$,[5]
$4(NH_4)_2C_2O_4.CdC_2O_4.8H_2O$,[6]
$4(NH_4)_2C_2O_4.CdC_2O_4.7H_2O$.[6]

In view of the number of very improbable salts in the above list, it seemed desirable to test for the formation of these double salts by the solubility method. Varying mixtures of ammonium oxalate with each of the others were treated with water and warmed, then placed in the thermostat and shaken at 25°. Solutions and residues were analyzed. Ammonia was determined, as before, by distilling from sodium hydroxide into standard acid and total oxalate by titration with perman-

[1] Souchay and Lenssen: Ann. Chem. (Liebig), **99**, 31.
[2] Kayser: Pogg. Ann., **60**, 140.
[3] Brandes: Schweig. Jour., **27**, 18. Ref. Watts' Dict., **3**, 649.
[4] Beilstein, 3rd Ed., **1**, 642. This refers to Kayser's salt, but is incorrectly quoted.
[5] Souchay and Lenssen: Ann. Chem. (Liebig), **103**, 308.
[6] Rammelsberg: J. prakt. Chem., **63**, 378.

ganate. The amount of each oxalate could then be calculated. The results obtained are in the following tables :

Table IV.—Solubility of Ammonium and Magnesium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	MgC_2O_4 in solution.	$(NH_4)_2C_2O_4$ in residue.	MgC_2O_4 in residue.	Residue contains:
1	5.59	0.60	2.01	73.92	$(NH_4)_2C_2O_4.H_2O$
2	5.32	0.57	81.70	4.66	and $MgC_2O_4.2H_2O$
3	5.07	none			$(NH_4)_2C_2O_4.H_2O$

Table V.—Solubility of Ammonium and Zinc Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	ZnC_2O_4 in solution.	$(NH_4)_2C_2O_4$ in residue.	ZnC_2O_4 in residue.	Residue contains:
1	6.39	1.64	1.19	80.33	$(NH_4)_2C_2O_4.H_2O$
2	6.11	1.51	39.72	43.91	and
3	6.17	1.69	61.78	23.53	$ZnC_2O_4.2H_2O$
4	6.11	1.58	83.92	3.27	
5	5.07	none			$(NH_4)_2C_2O_4.H_2O$

Table VI.—Solubility of Ammonium and Cadmium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	CdC_2O_4 in solution.	$(NH_4)C_2O_4$ in residue.	CdC_2O_4 in residue.	Residue contains:
1	5.08	0.29	8.71	71.33	$(NH_4)_2.C_2O_4.H_2O$ and
2	5.05	0.27	77.06	10.69	$CdC_2O_4.3H_2O$
3	5.07	none			$(NH_4)_2C_2O_4.H_2O$

In each of the above tables it will be noticed that the composition of the solution remains constant, though the residues vary between extreme limits, showing that no double salt has formed. On account of the very slight solubility of magnesium, zinc and cadmium oxalates, in the presence of the saturated solution of ammonium oxalate, it is, further, very probable that no double salts of these oxalates exist at any temperature.

SHEFFIELD CHEMICAL LABORATORY,
NEW HAVEN, CONN.,
March, 1905.

REVIEWS.

TECHNO-CHEMICAL ANALYSIS. By G. LUNGE, Professor at the Eidgenössische Polytechnische Schule at Zurich. Authorized translation by A. I. COHN. New York: John Wiley & Sons. First edition. 1905. pp. 136. Price, $1.00.

The scope of this little book is explained as comprising the examination of raw material for chemical factories and other technical industries, the operative control of chemical factories by chemical and physical means and the examination of the end-products, with respect to the properties which have an important bearing on their employment. In many cases empirical methods are used, very often, however, the methods employed in scientific chemical analysis must be adopted, with every attention to extreme accuracy.

The subjects treated are gas analysis, fuels, acids, soda, carbonated lyes, chlorine industry, potassium salts, clay and cement industry, artificial manures, gas and ammonia manufacture, calcium carbide, coal tar industry, mineral oils, oils and fats, soaps, glycerine, sugar, alcohol manufacture, vinegar, wine, beer, tanning and dyeing.

While excellently well adapted to the use of technical chemists, Professor Lunge's book seems rather brief and condensed, but, doubtless, is what is wanted for general use. When employed in connection with the author's larger work, "Chemisch-Technische Untersuchungsmethoden," to which frequent reference is made, it would fill every requirement. E. R.

A SCHEME FOR THE DETECTION OF THE MORE COMMON CLASSES OF CARBON COMPOUNDS. By FRANK E. WESTON, B.Sc., F.C.S. London: Longmans, Green & Co. 1904. pp. 56. Price, 2 shillings.

The contents of this book embody the results of seven years' experience and it has been prepared for the use of students intending to submit themselves to two English examining boards. After various preliminary observations, the student is directed to ascertain what elements are present in the compound he is working with, the result he obtains will place it in one of 10 large groups, which are subdivided into 42 smaller ones. As an example, compounds containing carbon, hydrogen and nitrogen are divided into "amines, diamines, hydrazines, alkaloids, pyridine and quinoline and pyrrol and alkyl." This is, presumably, a misprint. The idea of giving students of organic chemistry some work of a qualitative analytical nature is good and has suggested itself to others, as is

shown by the preparation of Mulliken's book[1] on the subject, but the present little volume is hardly likely to encourage instruction in this direction. The tests are very often vague, meaningless and, not infrequently, incorrect, as the following examples show: "Deep red coloration (with concentrated sulphuric acid) indicates certain glucosides," p. 5. "To detect *triple* bond, carefully mix substance with ammoniacal Cu_2Cl_2 solution; when colored, insoluble body will be produced," p. 9. "All hydroxy acids when acted on with acid chloride (*sic*) yield esters in which acid residue enters the alcohol—OH group," p. 17. "Only those hydrazones containing an OH group in the α-position to the hydrazine radicle are capable of forming osazones," p. 39. The apparatus illustrated is very antique and inconvenient, except where it is utterly trivial. There is no index. The book must be described as an unhappy attempt to help a rather useful cause. J. B. T.

THEORETICAL CHEMISTRY FROM THE STANDPOINT OF AVOGADRO'S RULE AND THERMODYNAMICS. By PROF. WALTHER NERNST, PH.D., of the University of Göttingen. Revised in accordance with the fourth German edition. By R. A. LEHFELDT, D.Sc. London and New York: Macmillan & Co., Limited. 1904. pp. 771. Price, $3.75.

The appearance of the first edition of this important work has already been noticed.[2] The book has now been carefully revised and brought up to date, it is, of course, not adapted to the beginner, but is indispensable to every advanced student of physical chemistry, as well as to every teacher of the subject.

It is a matter for deep regret that we cannot get a satisfactory translation into English of such a book. The present translator states in his preface that "I have translated all the new matter contained in the fourth German edition and revised certain parts of the old, in the endeavor to free the book from any mistakes and ambiguities that a first edition is so liable to contain. The bulk of the old text, however, remains as it was."

The defective nature of the original translation is well known. If we examine the new one we find many of the old defects still remaining, as we should expect from the above admission on the part of the present translator. Indeed, we can scarcely turn to a page where we do not find some violation of good, idiomatic English. In some cases this violation is so glaring as either to obscure the meaning or to leave it ambiguous. The number of examples is so large that it would require an extended review to point them out.

[1] THIS JOURNAL, 32, 404.
[2] *Ibid.*, 17, 541.

For these reasons the student and teacher are advised to purchase the book in the original German. H. C. J.

THE VARNISHES OF THE ITALIAN VIOLIN-MAKERS OF THE XVI. AND XVII. CENTURIES. By GEORGE FRY, F.L.S., F.C.S. London: Stevens & Sons, Limited. 1904. pp. xii + 170. Price, $1.50.

It appears that Mr. Fry, who is a chemist of long experience, is also a musician. In 1901 his attention became fixed on the varnishes used by the famous old violin-makers to such a degree that he undertook to find out how they were prepared. These varnishes are very elastic and not very hard; hence they cannot be alcoholic spirit varnishes; the general opinion is that they are either oleoresinous or turpentine-spirit varnishes. The author, it seems, knew nothing about the practical part of making or using varnish in general, but he invented, first, a theory that the violin-makers used such products as were naturally found in their own vicinities, namely, colophony, turpentine, turpentine-spirit and linseed oil; and second, varnishes made of these materials resembling those on the old instruments. These old varnishes are from red to brown in color; modern practice is to obtain these tints by dissolving coloring-matter in the otherwise pale-yellow varnish. The author, in brief, dissolves his resinous matter in turpentine spirit and to this adds strong nitric acid, heats the mixture until the color is developed, then adds linseed oil and more turpentine-spirit, if necessary. In general, he uses half as much oil as colophony. These varnishes he declares to be durable, but as his experiments extended over only 2 or 3 years and as it is evident that he was not much accustomed to testing varnishes, this should be regarded as being, as yet, unproved. The book is interesting and valuable; it brings together a large amount of information regarding violin varnishes, while the products invented by the author are, at least, novel. The present reviewer (a varnish-maker) does not believe such varnishes are valuable, but as he has not tried them this is only an opinion; certainly there is no proof that they were known in the past, while there is a large body of evidence to show that amber or other similar varnishes were used for the purpose. Nitric acid, while it has not been employed in this way, has been tried in varnish-making before, but was found to be of no use; no colophony varnish of permanent value has yet been made, although such varnishes are of great antiquity. The trouble with the violin-varnish problem is that it is of no commercial importance; the expert varnish-makers devote their ingenuity and knowledge to make their products as nearly colorless as possible. Beautiful deep-red

and brown varnishes may be made of amber and we know that they were made in Italy at the time in question, also at least one learned contemporary stated that they were used on lutes and other musical instruments.

The book is clearly and simply written; it is frankly the *ex parte* argument of a man who is convinced that he is right; the experiments are given in sufficient detail; it contains a bibliography of the subject; it has a very full table of contents, but no index. Many singular and almost uniformly erroneous beliefs about oleoresinous varnishes are stated as facts, but the author is evidently honest and straightforward and a careful and ingenious experimenter. A. H. SABIN.

PRACTICAL EXERCISES IN CHEMICAL PHYSIOLOGY AND HISTOLOGY. Arranged by H. B. LACEY, Head of the Biological Department of the South-Western Polytechnic, Chelsea, and C. A. PANNETT, B.Sc, London, Lecturer in Physiology at the South-Western Polytechnic, Chelsea. Cambridge: W. Heffer & Sons; London: Simpkin, Marshall & Co. 1904. pp. 112. Price, 2 shillings, net.

This little manual was devised for English students who are to present themselves for certain examinations. The first 56 pages are devoted to chemical experiments and the latter part to histology. The directions are very explicit and evidently were intended for students who have had no training whatever and merely desire to get quickly some idea of the subject and to pass a good examination in it. A. S. L.

EXERCISES IN PRACTICAL PHYSIOLOGICAL CHEMISTRY. By SYDNEY W. COLE, M.A., Additional Demonstrator in Physiology, Cambridge University. Cambridge: W. Heffer & Sons; London: Simpkin, Marshall & Co. 1904. pp. 152 Price, 5 shillings, net.

This manual is very clearly written and the experiments well described. It contains no special features except a new color test for lactic acid, by F. C. Fopkins, which will probably prove useful.

The book is presented in nice, readable form and commends itself for a brief laboratory course. A. S. L.

CHEMICAL STATICS AND DYNAMICS, Including the Theories of Chemical Change, Catalysis and Explosions. By J. W. MELLOR, D.Sc. B.Sc., Author of Higher Mathematics for Students of Chemistry and Physics. London, New York and Bombay: Longmans, Green & Co. 1904. pp. 528. Price, $2.00.

The author of this book is well known in connection with the manual referred to above. The same valuable characteristics that appear in the "Higher Mathematics for Students of Chemistry and Physics," manifest themselves in the present work. The material is well selected and treated in a clear and

concise manner. The work comprises 14 chapters: Introduction; Homogeneous Chemical Reactions; Homogeneous Side Reactions; Homogeneous Opposing Reactions; Homogeneous Consecutive Reactions; The Beginning of a Chemical Reaction; Heterogeneous Reactions; Equilibrium and Dissociation; Electrolytic Dissociation; Catalysis and the Theory of Chemical Change; Fermentation; The Influence of Temperature on Chemical Reactions; The Influence of Pressure on Chemical Reactions; Explosions.

Not the least valuable portion of this book is the large number of references to the literature given at the bottom of the pages. It would be a step forward if this principle were adopted in all text-books of an advanced character, at least in physical chemistry.

The book, as a whole, is of the same high character as Findlay's Phase Rule, in this same series. The series, edited by Sir William Ramsay, will doubtless prove to be a valuable addition to physical chemical literature. It is, however, to be regretted that one of the most interesting and important sections of the science—electrochemistry—should have been treated so much less satisfactorily than the remainder. H. C. J.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY AND BLOWPIPE ANALYSIS FROM A PRACTICAL STANDPOINT. By ALFRED J. MOSES, E.M., PH.D., and CHARLES LATHROP PARSONS, B.S. Third enlarged edition. New York: Van Nostrand Co. 1904. Price, $2.50 net.

Earlier editions of this well-known text-book have been reviewed in THIS JOURNAL as they appeared.[1] The present edition follows, in general, the design of the previous issues, but has been considerably enlarged; the chapter on Crystallography has been entirely rewritten and the chapter on Descriptive Mineralogy has been carefully revised and, in parts, rewritten. The text has also been more fully illustrated by the addition of 30 or 40 half-tones, which assist in bringing out the characteristic clustering of different minerals. The substitution of minerals for models in the crystallographic portion is likely to add to the interest of the student and to make him more familiar with a few typical minerals of strong crystallizing power. There are numerous minor criticisms suggested by a perusal of the book, but it will doubtless continue to prove its usefulness in the field to which it is devoted—the discussion and determination of minerals from a practical standpoint.

E. B. M.

[1] THIS JOURNAL, 17, 629 (1895); 25, 250 (1901).

THE RECENT DEVELOPMENT OF PHYSICAL SCIENCE. By WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S., Fellow of Trinity College, Cambridge. Philadelphia: P. Blakiston's Son & Co. 1904. Price, $2.00 net.

This interesting book might fairly be said to be the work of the Whetham family, since Dr. Whetham states, in his preface, that he "wishes especially to thank his wife for continual correction both of the manuscript and of the proof-sheets and his sister for help with the index." The aim of the work can be shown by a quotation from the preface. "It happens that an acquaintance with the knowledge newly acquired in one department of science is necessary for the study of another; indeed the phenomena which need for their interpretation the methods of two branches of science have proved often the most fruitful field of inquiry. For reasons such as these it has been thought possible that a short account of some of the important investigations now being carried on in the physical laboratories of the world, might prove useful to students of science in general; while it is hoped that, by treating the subjects as far as possible without technical language, the book may also appeal to those, who with little definite scientific training, are interested in the more important conclusions of scientific thought."

The reviewer agrees absolutely with the author in both of these matters. Any one who has had to do with the training of young men in science has been painfully impressed with the narrowness of their knowledge. This may be necessary at first, but if not overcome, later, by the individual, is fatal to his success. Bunsen said, in his day, that "a chemist who is not a physicist is nothing," and this holds much more rigidly today than in the time of Bunsen.

In reference to bringing the main results of scientific investigation to the level of the intelligent public, much might be said. In the opinion of the reviewer men of science, in this respect, often neglect a pressing duty. The chief aim of scientific investigation is the discovery of generalizations, but why do we wish to discuss these so-called Laws of Nature? It is for the good of mankind—not the material, but the intellectual good. That the greatest good should be achieved by scientific investigation, the results should be accessible to the greatest number. This can be accomplished only by books such as the one under discussion.

It is to be regretted that men of science sometimes look upon such work as not quite up to their standard. In taking such a view they greatly limit the sphere of their usefulness to the

race. It is a fair question to ask whether the college student always represents the best intellect and whether there are not as strong intellects outside as inside the university? Tyndal did much work of the semi-popular kind, both in his lectures and his books and it is to be hoped that work of this character will be greatly increased in the future. In this way only can that large number of highly intelligent people, who, for one reason or another have been barred from a university career, be shown the true grandeur of scientific investigation.

The reviewer must take exception to what Dr. Whetham says on page 30 and following, in reference to "Laws of Nature." The discovery of generalization or "Law" is the highest aim of the investigator. Beyond this, at present, he cannot go. Whether these generalizations, in any case, correspond to ultimate truths we do not know and have no means, at present, of finding out. It is, therefore, much more nearly correct to say that the highest aim of the scientific investigator is the discovery of generalization, than to say that it is the discovery of truth.

The book discusses; The Philosophical Basis of Physical Science; The Liquefaction of Gases and the Absolute Zero of Temperature; Fusion and Solidification; The Problems of Solution; The Conduction of Electricity through Gases; Radio-Activity, Atoms and Ether; Astro-Physics.

H. C. J.